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A Study of the Alkali Resistance of the Pentosans in Aspenwood

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A STUDY OF THE ALKALI RESISTANCE OF THE PENTOSANS IN ASPENWOOD

A thesis submitted by

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INTRODUCTION

The hemicelluloses of trembling aspen are composed mainly of pentosans (xylan and araban), together with smaller amounts of uronic acids, mannan, galactan, and glucan. The amount of araban is also rather small, so that aspen hemicelluloses may actually contain as much as 65 to 70% xylan.

The term "hemicellulose" was first applied by Schulze (1) in 1891 to the cell-wall components of plant materials which (a) enter solution readily in hot dilute mineral acids, with the formation of simple sugars, and (b) which are soluble when heated with dilute alkalies. Today this term is also used to designate the polysaccharides which can be extracted from a wood holocellulose by means of cold concentrated alkalies. Several excellent papers by Wise (2-4) on the hemicelluloses are available which give a thorough summary of the chemistry, analysis, and importance of the hemicelluloses. He has presented a diagrammatic scheme of the interrelationship of the various cell-wall components of wood in an attempt to clarify the somewhat confused nomenclature. The importance of the careful standardization of procedures and the careful definition of the various terms was strongly emphasized.

Since the pentosans are readily hydrolyzed with hot dilute mineral acids, they are, by one definition (a), a part of the hemicelluloses. However, a certain portion of the xylan in aspenwood (and other woods) remains in the analytically defined alpha-cellulose fraction. In the case of hardwood kraft pulps, even more of the xylan is resistant to alkaline extraction. By the second definition (b), this resistant xylan

is not a part of the hemicellulose fraction but belongs to the alpha-cellulose.

It is difficult to say just where alpha-cellulose ends and hemicellulose begins. It is certainly helpful to standardize the experimental conditions used for holocellulose and hemicellulose preparation, and, for any piece of work, to make it perfectly clear to the reader what those standards are. Nevertheless, such a procedure will not serve to solve the problem. A study of this phenomenon of alkali resistance of pentosans as affected by various conditions of holocellulose and pulp preparation and under various conditions of alkaline extraction should prove to be very enlightening.

PRESENTATION OF THE PROBLEM

The general problem can be stated as a study of the factors which affect the resistance of aspenwood pentosans to cold alkaline extraction. This study included the various methods of preparing the wood for extraction, such as kraft pulping, holocellulose preparation, bleaching, etc., as well as the conditions of the alkaline extraction itself.

The above statement is a good generalization of the thesis work in its final form. However, the problem as it was presented at the onset of the experimental work was much more specific. It was taken from certain of the analytical data of March (5), who found a difference between the alkaline resistance of pentosans in a bleached kraft pulp and that of the pentosans in a holocellulose, both prepared from aspenwood. The alpha-cellulose from the bleached kraft pulp contained 6.9% pentosan, whereas the alpha-cellulose from chlorite holocellulose contained only 1.2% pentosan. These results are paradoxical because the sodium chlorite delignification procedure is generally believed to be rather gentle in its action on carbohydrate material, whereas the kraft process is anything but gentle.

Before the problem was given final approval as a thesis topic, it was required that March's work be repeated on a new sample of aspenwood to corroborate his data. These experiments produced a kraft pulp alpha-cellulose which contained 6.6% pentosan and an analytical alpha-cellulose from chlorite holocellulose which contained 2.3% pentosan. This difference

was not quite as great as that obtained by March, but it was considered sufficient to warrant further study.

Specifically, the problem was to attempt to discover why an alpha-cellulose from a bleached aspen kraft pulp should contain more pentosan than one from an aspen chlorite holocellulose.

HISTORICAL REVIEW

The resistance of pentosans to alkaline purification has received considerable attention in the past because of its industrial importance to the dissolving pulp industry. Highly purified alpha pulps with low pentosan content are required for the viscose, acetylation, and nitration processes. Bleached sulfite softwood pulps purified by cold concentrated alkaline extraction have been the most extensively used because they exhibit a greater purity than dissolving pulps prepared from hardwood sulfite and softwood or hardwood alkaline-cooked pulps.

However, hardwood soda or kraft pulps, although the most difficult to purify, offer two important advantages over softwood sulfite pulps. First, the hardwoods represent a great, relatively untapped source of raw material, available at lower cost than the softwoods because of less competition with the paper pulp industry. Fiber length is not of great importance to the dissolving pulp industry. Second, the alkaline cooking processes produce pulps with much narrower ranges of molecular weight distribution than the sulfite process. This is a decided advantage in the regeneration of cellulose from solution. The use of hardwood pulps has spurred interest in the so-called "resistant" pentosans and their removal by various purification procedures. Prehydrolysis followed by alkaline cooking has been found to be a satisfactory means of making these hardwood pulps easier to purify, i.e., to remove pentosans.

The amount of resistant pentosan may depend upon the kind of raw material, the delignification process, the bleaching process, the purification process, and the procedure used to determine resistant pentosan.

The point which requires emphasis, however, is the tendency when dealing with one specific raw material to state that a certain pulping process or other treatment "increased the amount of resistant pentosan". It is just as likely that the treatment which produced the reference material containing the smaller amount actually decreased the amount of resistant pentosan. Since the true amount of resistant pentosan cannot be determined, it must be remembered that any statements as to a given treatment increasing or decreasing the resistant pentosan are only relative.

The resistance which portions of the pentosans show toward alkaline extraction and to a lesser but definite extent toward acid hydrolysis, led many investigators to conclude that a linkage of some sort must exist between these resistant pentosans and the cellulose in the wood fibers. The nature and type (chemical or physical) of this linkage are still obscure, and various workers have expressed different views as the results of their experimentation.

One of the first publications dealing with resistant pentosan was that of Schmidt and co-workers (6) presented in 1930. They found what they considered to be a rigidly observed stoichiometric relation between resistant xylan and cellulose of red beechwood of one anhydroxylose unit in the resistant xylan to three anhydroglucose units in the cellulose. They interpreted these data as proof of a chemical linkage between cellulose and xylan. However, the experimental procedures which they used to obtain these data made their conclusions rather doubtful. They obtained the "structural substance" (holocellulose) of the wood by alternate treatments with aqueous solutions of chlorine dioxide gas and sodium sulfite.

The "easily soluble xylan" was then removed by extraction with 0.2% sodium hydroxide solution. The residue was then considered to consist of "cellulose plus difficultly soluble xylan" (d. s. xylan). The d. s. xylan was then determined as the weight lost on extraction of the residue with 5% sodium hydroxide containing 3% sodium chloride. The residue was termed "cellulose". The ratio of "d. s. xylan" to "cellulose" was calculated by first converting the weights to equivalent xylose and glucose anhydride. They consistently obtained the ratio of 1:3. The two most obvious errors in this interpretation are that in a complex mixture such as holocellulose the "d. s. xylan" is not all xylan, and the "cellulose" still contains a more resistant xylan than Schmidt's "d. s. xylan".

In 1934 Lüdtke (7) applied the procedures of Schmidt to bamboo and beechwood and was unable to check some of his work. Lüdtke felt that the cellulose-to-xylan ratio of 3:1 was just an accidental average. He proposed an organized growing relationship with the chief components existing in the free state in opposition to Schmidt's ester linkage theory.

Jayme (8) repeated the Schmidt separation process on the holocellulose produced with sodium chlorite from beechwood. He obtained a molar ratio of anhydroglucose to anhydroxylose of 2.84:1 which agreed only approximately with the ratio of 3:1 found by Schmidt. However, Jayme showed that the 5% sodium hydroxide-insoluble residue which Schmidt called "cellulose" still contained 6.44% pentosan. He also concluded that the integral ratio between cellulose and pentosan found by Schmidt was accidental and was caused by the choice of sodium hydroxide concentrations

used and an assumption that the cellulose residue no longer contained pentosan.

Voss (9) ascribed the resistance of pentosans to alkaline extraction to the particular orientation of the fiber building units in the cell wall. According to him the cellulose chains are surrounded by a dense layer of xylan chains.

Jayme (8) presented a picture similar to that of Voss. He felt that the cellulose micelles consist of a nucleus of pure cellulose, at the surface of which the pentosan, mannan, etc., are firmly built into the cellulose chains. These built-in constituents are difficultly soluble in alkali and are found in the alpha-cellulose residues. The exact nature of the linkage was not disclosed, but Jayme apparently referred to a chemical linkage since he stated that these polyoses can be removed only by a hydrolysis in which the remaining cellulose chains must possess a lower degree of polymerization because the other polysaccharide portions which interrupt them are dissolved out.

Asthury, Preston, and Norman (10) advanced the view that the xylan molecules in the fibers participate in the micelles and are oriented in the same direction as the cellulose chains. They found that the removal of xylan from fibers of high xylan content merely made their x-ray photographs more like those of fibers of low xylan content which show a more perfect state of crystallization. They believed that the results of their experiments favored the view that the incorporation of xylan is a sort of mixed crystallization. Pentosan chains would be retained by secondary valence forces in the oriented regions, similar to those which operate between adjacent cellulose chains.

Norman (11) presented what he believed to be chemical evidence of the above view that the pentosan molecules participate in the cellulose micelles. The xylan unit differs from the glucose unit in cellulose only in that the terminal $-CH_2OH$ group is missing. Both are in the pyranose ring form. They are therefore of the same size and could occupy the same space longitudinally. These cellulosans, as they are called by Norman, are probably laid down with the cellulose as it is formed and are retained by secondary valence forces. He prepared Cross and Bevan cellulose from wheat straw. Direct extraction with 4% cold sodium hydroxide produced a residue which contained 8.3% xylan. Samples of the original cellulose were then dissolved in cuprammonium and by the viscose process. Extraction of the regenerated celluloses with 4% cold sodium hydroxide gave residues which contained 0.4 and 1.1% xylan, respectively. No equivalent increase in availability of hexosan material occurred. Acid hydrolysis treatment was also found capable of easily removing the resistant xylan; 3% sulfuric acid at 100°C. for one hour proved to be satisfactory. After the solution and regeneration of the cellulose, the organized arrangement is largely destroyed, and the secondary valence forces between cellulose and xylan are no longer in effect. Thus the xylan can be more readily extracted.

The possibility of chemical combination is not ruled out by Norman (12,13). He suggested that there may be mixed chains of xylan and cellulose, or more accurately, of xylose and glucose. The presence of a few such chains might account for the extreme stability of a small portion of the xylan which resists extraction by long boiling with 10% sodium hydroxide. Some measure of cross-bridging between xylan chains

and cellulose chains, providing a three-dimensional structure, may also be possible.

Meyer (14) stated that there are certain indications that some of the hydroxyl groups in native cellulose are masked, perhaps by the formation of esters with carboxyl groups of neighboring chains. The x-ray diagram clearly shows that bundles of pure cellulose chains are present in untreated fibers; these may be linked chemically at their edges with substances such as xylan or other hemicelluloses. Certain amounts of these associated substances may also lie between the ordered regions. He pointed out that neither the x-ray analysis nor chemical analysis is perfect. The x-ray studies do not rule out the possibility of chemical linkages at the edges of the micelles, whereas chemical methods do not show whether sugars and uronic acids obtained on hydrolysis were originally in the same molecule or in different chains. Meyer also suggested the possibility that the polyuronic acids may form a cement between the cellulose micelles, chemically linked together around micelles, or surrounding groups of micelles.

Sisson (15) supported the view that mixed crystallization may occur at the surface of the crystallites between cellulose and noncellulose material. He stated that the bonding would thus be of a secondary valence type rather than of a primary valence type.

In 1933 Klingstedt (16) studied the difference in response of alkali-digested pulps and sulfite pulps to the action of caustic soda. He found no difficulty in removing the furfural-forming components from spruce sulfite pulp with 17-18% sodium hydroxide. However, alkali-digested

pulps could not be completely freed of these substances by a similar extraction. He found that 11% by weight of sodium hydroxide exerted the greatest dissolving effect on pentosans. An alpha-cellulose from aspen sulfate pulp prepared by a one-hour extraction with 17% sodium hydroxide contained 10.9% xylan.

Lindpainter (17) presented a very thorough discussion of the significance of pentosans in rayon pulps and their removal by alkaline purification. He proposed that the behavior of a pulp on alkaline purification depends upon three factors: (1) The strength of the cellulose-pentosan linkages whatever their nature may be; (2) the polydispersion or molecular weight distribution; and (3) the influence of morphological and biological structure of the fibers. According to him, acidic pulping is classed as intensive disintegration and results in weak cellulose-pentosan linkages and the formation of considerable lower-molecular weight cellulose (high polydispersion). The removal of pentosan is easily accomplished but may be accompanied by a considerable loss of cellulose. On the other hand, alkaline pulping is a protective disintegration process. The cellulose-pentosan linkage is very strong, and the amount of low-polymer cellulose is small. Because of the low polydispersion, the pulps are more suitable for rayon manufacture, and less loss of cellulose occurs on alkaline purification. However, a suitable purification procedure must be found to break the cellulose-pentosan linkage. Lindpainter claimed that 2.5 N (9.1% by weight) sodium hydroxide exerts the greatest swelling and solvent action on cellulose.

Dolmetsch, Franz, and Correns (18) studied the influence of the morphological structure of pulps upon their reactions and swelling properties in various reagents. They observed the cracks or fissures which appear in pulp fibers during strong swelling and discovered characteristic morphological differences between pulps prepared by alkaline and acidic treatment. In alkaline pulping, the morphological structure of the tracheids was scarcely attacked insofar as their behavior on subsequent swelling was concerned. Crack formation did not occur on swelling with 18% sodium hydroxide. The inner layer of the secondary wall appeared on strong swelling as an apparently homogeneous gel which distended the difficultly soluble outer layer of the secondary wall with spiral cleavage along its spiral structure, which was retained in full strength. Pulps obtained merely by alkaline defibration and chlorination also did not show any crack formation. The effect of acid pulping agents, prehydrolysis, or acidic retreatment of alkaline-cooked pulps could be recognized by the formation of transverse and longitudinal cracks in swelling which increased with the degree of hydrolysis. The spiral structure of the outer layer of the secondary wall disappeared to the same extent. It was the view of these workers that their results explained in a simple way the differences between sulfite and sulfate pulps which are often observed and also the advantageous effect of prehydrolysis on sulfate pulps which are intended for dissolving pulps. To attain paper pulps with high mechanical strength, the sulfate process, which protects the morphological structure of the fiber, seems to be especially suitable.

The first reference which could be found reporting an "increase" in the amount of pentosan associated with the cellulose due to alkaline pretreatment of the wood was an article published in 1930 by Campbell and Booth (19). Working with an 60-100 mesh wood meal from English oak, they found that the Cross and Bevan cellulose content of the green wood was 53.0% and that it contained 26.0% pentosan based on the cellulose. When the wood meal was first extracted with hot 1% sodium hydroxide solution for one hour and dried, the Cross and Bevan cellulose content increased to 53.9% with an increase in its pentosan content to 30.6%. Air drying of the wood meal also resulted in an increase in the pentosan content of the cellulose, but it was not as pronounced as that caused by alkaline treatment. Campbell and Booth made no attempt to explain the increase in pentosan content of the cellulose caused by alkaline pretreatment but stated that it would appear that an increase in the pentosan content of the Cross and Bevan cellulose after alkaline extraction is characteristic of hardwoods.

Mackney (20) studied the effect of alkaline pretreatment on Eucalyptus regnans. The untreated wood had a Cross and Bevan cellulose content of 61.8% and contained 20.9% xylan based on the cellulose. Pretreatment of the wood with hot 0.16% sodium hydroxide increased the Cross and Bevan cellulose to 63.2% (containing 22.6% xylan), whereas pretreatment with hot 1% sodium hydroxide produced 61.0% Cross and Bevan cellulose (containing 23.0% xylan). In the discussion of the above data, Mackney made the following statements: "A logical explanation of these facts is difficult to reach. Probably there is some effect arising through the breaking of a lignin-hemicellulose bond by alkaline treatments of

moderate severity. Prior to the rupture of such a bond it is conceivable that removal of lignin by chlorination and sulfite treatment would involve the removal of a certain amount of hemicellulose which is otherwise stable to alkali treatment. After breaking of the bond the lignin is more readily removed and the hemicellulose is retained by the cellulose as a relatively resistant fraction. In fact this material is of such stability it is retained while attack on the cellulosic material occurs."

McKinney (21) also expressed the opinion that alkaline cooking increases the amount of alkali-resistant pentosan. He compared sulfite cooking, kraft cooking, and prehydrolysis-kraft cooking as to their effect on the acetylating properties of wood pulps. An alpha-cellulose prepared from a hardwood kraft pulp produced an extremely hazy acetate. Sulfite prehydrolysis followed by kraft cooking gave a satisfactory acetate pulp. However, by reversing this procedure and giving a sulfite cook to a kraft pulp he was not able to produce a satisfactory acetylating pulp. He proposed the theory that "anhydro-hemicelluloses" are formed during alkaline cooking which are very resistant to subsequent treatment with acid or alkali.

Keller (22) reported that hypochlorite bleaching caused a greater reduction in resistant pentosans than did acid hydrolysis. He determined resistant pentosans as those remaining in the pulp residue after two extractions with cold 6.5% (by weight) sodium hydroxide. In a personal communication he stated that 6.5% sodium hydroxide exerted the greatest dissolving power on pentosans.

In a further study Keller (23) found that heat drying at 105°C. increased the resistant pentosan content of a large variety of pulps. Beating of the pulps in a Lampén mill reduced the resistant pentosan content. He postulated that drying and beating influence the surface as well as the chemical properties of the fibers. The final amount of resistant pentosan is the net effect of the simultaneous action of opposing or supplementary forces acting during the particular treatment being given.

EXPERIMENTAL PROCEDURES

RAW MATERIAL

PREPARATION

The wood used throughout the thesis work was obtained from an aspen tree (Populus tremuloides) which was cut behind The Institute of Paper Chemistry in June, 1950. Its diameter at breast height was 6½ inches, and the approximate age was 20 years. The tree was cut into six 2½- to 3-foot sticks which were then peeled and freed of knots as well as possible by means of a hatchet.

Four of the sticks were converted to half- to one-inch chips in the Institute chipper. The chips were air dried, screened to remove fines and oversize chips, thoroughly mixed, and stored in large paper bags. One stick was saved for possible future use, and one was converted to coarse sawdust with a small circular saw. The sawdust was mixed, air dried, passed through the No. 1 Wiley mill, and screened. The material which passed a 30-mesh screen but was retained on a 50-mesh screen (30-50 mesh fraction) was saved for the bulk of the experimental work. The coarse material was given a second pass through the Wiley mill and rescreened. The 50-70 mesh fraction was also saved in case a use for it should arise.

In the course of the work, more wood meal of various mesh sizes was required. This was prepared from the chip supply by passing them through the Wiley mill and screening the resulting wood meal to obtain the desired fractions.

Wood shavings were also used as a raw material for several experiments. These were obtained from the unused stick of aspen. The thin, hand-made shavings were obtained by means of a sharp carpenter's plane. This time-consuming process was abandoned in favor of the use of a power-driven planer or jointer. It was experimentally determined that the small, thin shavings prepared in this manner could be converted to pulps which were very similar to those obtained from the hand-made shavings.

ANALYSIS OF RAW MATERIAL

The air-dried 30-50 mesh meal was analyzed by the standard Institute of Paper Chemistry procedures. All analyses except those for extractives and ash were made on the extractive-free wood meal. The extractive-free wood meal was prepared for analysis in a Soxhlet extractor by alcohol extraction and subsequent water extraction of two 50-gram batches of air-dried wood meal of known moisture content. The extractives removed from the above material were determined by evaporation and oven drying. Pentosan was calculated as xylan because of the small amount of araban present in aspenwood. The pentosan value was also corrected for uronic anhydride. The pentosan content as determined was 20.5%. Assuming 35% of the theoretical recovery of furfural from uronic anhydride, the correction was made by using the following formula:

$$\text{Xylan, \%} = 20.5 - \frac{4.7 \times 0.546 \times 0.35}{0.727 \times 0.88} = 19.1$$

where 0.546 is the theoretical conversion factor of uronic anhydride to furfural, 0.727 is the theoretical conversion factor of xylan to furfural, and 0.88 is the factor to compensate for incomplete conversion of xylan to furfural.

The results are presented in Table I.

TABLE I

ANALYSIS OF TREMBLING ASPENWOOD MEAL

	Extractive-free basis, %	Unextracted basis, %
Alcohol extractives		3.2
Water extractives		1.0
Total extractives		4.2
Holocellulose	86.4	82.8
Lignin	16.4	15.7
Alpha-cellulose[1]	53.9	51.6
Uronic anhydride	4.7	4.5
Pentosan[2]	19.1	18.3
Ash	0.4	0.4

[1] Not corrected for pentosan.
[2] Calculated as xylan, corrected for hydroxymethylfurfural and uronic anhydride.

Institute of Paper Chemistry Standard Methods used:

Holocellulose	Method 28
Lignin	Method 13
Alpha-cellulose	Method 421
Uronic anhydride	Method 25
Pentosan	Method 23a
Ash	Method 4

STANDARD PROCEDURES

CHLORITE HOLOCELLULOSE

The first point to emphasize is that distilled water was used throughout all the experimental work, with the exception of the wash water for the pulps prepared in the small digester.

All chlorite holocellulose preparations were made according to the method of Wise, Murphy, and D'Addieco (24) with air-dried, unextracted materials. The proportions of chemicals used were identical

with those specified and were determined by the amount of air-dried material to be delignified. For example, using 25 grams of wood meal in 800 ml. of water, three hourly additions of 3 ml. of glacial acetic acid and 7.5 grams of technical-grade sodium chlorite were made at temperatures of 70-80°C. The large-scale preparation was made with nine 150-gram batches of the 30-50 mesh wood meal, with the use of proportionate amounts of water, acetic acid, and sodium chlorite.

COOKING PROCEDURES

The following pulps were prepared from the aspen chips: (1) two kraft pulps, (2) a kraft semichemical pulp, (3) a soda pulp, and (4) a sulfite pulp. In addition, cooks were made on (1) cotton linters, (2) aspenwood meal, (3) chlorite holocellulose from wood meal, and (4) alpha-cellulose from wood meal.

All the above-mentioned cooks were carried out in a four-liter stainless steel digester equipped with a pressure gage, thermometer well, and relief valve. Heat was supplied by placing the digester in a wax bath heated by two Meker blast burners. The cooking liquors were prepared from c.p. chemicals and distilled water. The sulfite liquor was prepared by bubbling sulfur dioxide gas into a solution of c.p. sodium bisulfite of known concentration until the calculated weight increase had been obtained. The liquor was not analyzed.

When the cooking cycle was completed, the digester was removed from the wax bath and cooled by running a stream of cold water over it. The relief valve was then opened to reduce the pressure to zero, and the

cover was unbolted. The chips were dumped into a washbox, washed slightly with warm water, and converted to pulp in a Williams disintegrator. The pulps were then washed free of liquor with warm water, pressed as dry as possible, air dried, and stored in moisturetight bottles. The cooking conditions used for all cooks may be found in the appendix.

BLEACHING PROCEDURES

Technical-grade sodium chlorite and distilled water were used for the preparation of all bleached pulps. The unbleached pulps were Abbé milled prior to bleaching.

With a few exceptions (which will be described in the discussion of results), the pulps were bleached by a one-hour treatment of the standard chlorite holocellulose procedure already described. Different amounts of various pulps were often used, but the proportions of pulp, water, and chemicals specified for chlorite holocellulose preparation were always observed. Bleaching was carried out at 70°C. for one hour, after which the pulps were washed thoroughly with distilled water and acetone and air dried. In a trial experiment it was found that the use of an acetone wash did not change the resistant xylan content of the air-dried pulp.

ALPHA-CELLULOSE PREPARATION

The alpha-cellulose preparations were carried out for the principal purpose of determining resistant pentosans. The standard procedure adopted was similar to Institute Method 421, with the exception that the amount of pulp extracted was varied as desired. However, the

ratio of 25 ml. of 17.5% sodium hydroxide to 1 gram of air-dried pulp was always used.

The standard procedure can be briefly described as follows. An accurately weighed 10-gram sample of a bleached pulp or holocellulose of known moisture content was extracted with 250 ml. of 17.5% (by weight) sodium hydroxide for 45 minutes at room temperature. The mixture was then diluted with 250 ml. of water and filtered immediately by suction on a coarse sintered-glass Buchner funnel, washed with 2 liters of distilled water, soaked for five minutes in 200 ml. of 5% acetic acid, washed with two more liters of distilled water, and finally with acetone. The alpha-cellulose was then transferred quantitatively to a large weighing bottle and oven dried at 105°C. For further details reference should be made to Institute Method 421. After the yield determination was made, the alpha-cellulose was ready to be weighed out for resistant pentosan analysis.

Departures from this standard procedure were made for several reasons. During the studies of the effect of alkali type and concentration on alpha-cellulose yield and resistant pentosan content, various concentrations of sodium, potassium, and lithium hydroxide were substituted for the 17.5% sodium hydroxide. In these cases it was desirable to have only one concentration of alkali in contact with a pulp. At this point it was experimentally determined that the dilution step prior to filtration had a negligible effect on the resistant xylan content. Dilution was therefore eliminated from the procedure during these studies. The dilution step was also eliminated when the hemicelluloses were to be recovered from

the alkaline solutions. In certain cases larger quantities of alpha-celluloses were required for further experimentation, and oven drying of these materials was not desirable. The same ratio of pulp to alkali (1 gram to 25 ml.) was used, but the materials were air dried and stored in moisturetight sample bottles. The ovendry yields were calculated by determining the moisture contents of the bleached pulp and the resulting alpha-cellulose. In a test experiment it was found that oven drying the alpha-cellulose did not affect the resistant pentosan content; the same values were obtained for air-dried and oven-dried samples of the same material.

The large amount of alpha-cellulose for the kraft cook was prepared in batches from 650 grams of the 30-50 mesh chlorite holocellulose. The extraction was made with 16% potassium hydroxide for two hours at room temperature; 2000 ml. of alkali were used for each 100 grams of holocellulose. Potassium hydroxide was used because potassium acetate is more soluble than sodium acetate in the ethyl alcohol used for hemicellulose recovery.

HEMICELLULOSE RECOVERY

The hemicelluloses were recovered from one of the above batch extractions by the following procedure. The alkaline filtrate (not the washings) from the alpha-cellulose preparation was poured into four to five volumes of 95% ethyl alcohol which contained an excess of glacial acetic acid. The final mixture was slightly acidic to alk-acid test paper. The mixture was stirred thoroughly, and the hemicelluloses allowed to settle. Most of the supernatant liquor was removed by the use of a

siphon and the hemicelluloses were recovered by centrifugation. While in the centrifuge bottles, the hemicelluloses were washed three times with fresh 95% ethyl alcohol and twice with c.p. ethyl ether. They were then dried overnight in a vacuum oven at 50°C. and stored in a moisturetight sample bottle.

XYLAN ANALYSIS

All xylan analyses were run by the 12% hydrochloric acid distillation procedure. At the onset, the gravimetric and volumetric methods of determining the furfural in the distillate were compared on several alpha-celluloses. When both results were calculated as xylan and the same correction factor was applied to both, they were practically identical. It was therefore decided that the more rapid volumetric procedure would be used throughout the work. The details of the procedure are given in Institute Method 23a. The conversion factors specified in this procedure are such that the result is expressed as percentage xylan.

For all alpha-celluloses the correction factor of 0.9% was arbitrarily applied to correct the results for hydroxymethylfurfural arising from cellulose. A correction factor of 0.6% was arbitrarily subtracted from all results obtained for wood meal, holocellulose, and bleached and unbleached pulps. No correction was applied in the case of the hemicellulose preparation.

HYDROLYSIS PROCEDURES

Certain of the alpha-celluloses and the hemicelluloses were hydrolyzed to their constituent sugars and analyzed qualitatively by

means of paper partition chromatography. The first hydrolysis procedure used was essentially that of Institute Method 22 for mannan in wood or pulp with the following exception. After the neutralization with barium carbonate was completed and the mixture had been boiled for five minutes to expel carbon dioxide, it was filtered immediately, made slightly acidic with acetic acid, and concentrated in vacuo to a sirup. This sirup was then developed on a paper partition chromatogram with butanol-ethanol-water or ethyl acetate-acetic acid-water as the developer.

Later the more rapid method of Jones (25) was used. In this procedure the neutralization and concentration steps were eliminated. Instead the acidic solution was spotted directly on the paper chromatogram where it was concentrated by placing as many drops as desired on the same spot and allowing the water to evaporate between each drop. The chromatogram was then developed in butanol-pyridine-water. The pyridine neutralized the sulfuric acid, and the resulting pyridine salt remained near the starting line. The sugars themselves developed in the normal manner as though they had been spotted on the paper from neutral solution.

PAPER PARTITION CHROMATOGRAPHY

The sugar mixtures obtained by the above hydrolysis procedures were analyzed qualitatively by means of paper partition chromatography. The procedures used were based on those developed by Consden, Gordon, and Martin (26) and by Partridge (27). The separation was obtained on filter paper strips by allowing a suitable solvent, which was previously saturated with water, to flow over the paper in a closed container in which the air was saturated with the vapors of water and the solvent. Filter paper

contains 20-25% water under these conditions, and the separation depends upon the differences in partition coefficient of the sugars between the stationary water phase and the moving solvent phase. The process is essentially one of repeated fractional extraction.

Both Schleicher and Schuell No. 598YD and Whatman No. 1 filter paper strips were used for the chromatograms. The first is an extremely rapid paper and satisfactory for coarse separations of sugars present in fairly high concentrations. Whatman No. 1 is the most generally satisfactory paper for this type of work. It is suitable for quantitative separations and also for the careful separation and detection of the minor component sugars in a hydrolysis mixture.

An unknown sugar mixture was spotted alongside a known sugar mixture on a line ruled 8 cm. from the top of a 4-inch by 20- to 25-inch strip of filter paper. The top of this strip of paper was then placed in a trough containing the developing solution, and the strip was allowed to hang vertically in the sealed container. The container used was a stainless steel tank about 3 feet long, 2 feet wide, and 3 feet high. It had a hinged plate-glass cover which was tightly sealed by means of a rubber gasket and several swing bolts. This tank was thoroughly insulated with blanket insulation and elevated from the floor. Approximately a one-inch layer of the developing solution was placed in the bottom of the tank, and a large, heavy sheet of blotting paper was suspended in this solution. Capillary flow up the blotting paper therefore provided a large surface area for the saturation of the air in the tank with the vapors of the components of the solution. Later in the work, glass tanks which are available commercially were also used. These tanks would permit use of a

seven-inch wide strip of filter paper, but their operation was identical with the larger steel tank except that the sheet of blotting paper was not required to obtain saturation of the air with the various vapors.

Various developing solvents were used during the course of the experimentation, and these will be mentioned by name in the discussion of results. The four developers used are listed below. The numbers refer to the ratio of parts by volume of the respective components before they are mixed. After mixing, the first three are two-phase systems; the bottom layer is discarded, and the top layer is used as the developer. The ratio shown for the fourth developer produces a single phase so that separation is not necessary.

1.	Butanol-ethanol-water	4:5:1
2.	Butanol saturated with water	
3.	Ethyl acetate-acetic acid-water	3:1:3
4.	Butanol-pyridine-water	10:3:3

After the developing action had taken place for the desired time, depending upon the type of paper, the developer, and the amount of separation required, the strip was removed from the tank and allowed to dry in the air. It was then sprayed with the sugar reagent and heated in an oven at 105°C. for about five minutes. At the end of this time, the colored reaction products appeared on the paper where the sugars had been, and identification was made by comparing the known and unknown mixtures.

The most generally satisfactory spray reagent for sugars was found to be aniline hydrogen phthalate. It was made by dissolving 0.93 gram of aniline and 1.66 grams of phthalic acid in 100 ml. of butanol saturated with water. A crystal of stannous chloride was added to prevent

discoloration. It was sprayed onto the paper by means of a small glass and metal aspirator operated by compressed air. Aniline hydrogen phthalate differentiates between the hexose and pentose sugars by giving brown spots with hexoses and pink spots with pentoses. A second spray reagent used was p-anisidine hydrochloride. It gives brilliantly colored reaction products with the sugars. Its use was abandoned when it was found that the chromatograms were not permanent. In three to four days they were completely discolored and worthless. Chromatograms sprayed with aniline phthalate faded slightly but were still satisfactory after one and one-half years.

MISCELLANEOUS PROCEDURES

Uronic Anhydride

These determinations were carried out according to Institute of Paper Chemistry Method 25.

Permanganate Number

The permanganate numbers of various pulps were determined by employing Institute Method 410.

Ash Content of Hemicelluloses

The ash in the hemicellulose and xylan fraction was determined as sulfate according to Institute Method 109.

Viscosity of Xylan Fractions

The specific viscosities of the xylan fractions were determined by means of a #100 Ostwald-Fenske viscometer; 8% and 32% potassium hydroxide were used as the solvents. Concentrations of approximately 0.45 gram per

100 ml. were used. The specific viscosity was determined by the usual formula

$$\text{Specific viscosity} = \frac{\text{solution time - solvent time}}{\text{solvent time}}$$

and was converted to η_{sp}/c by dividing by the concentration (corrected for ash) of xylan.

SPECIAL PROCEDURES

MODIFIED THOMAS HOLOCELLULOSE PREPARATION

Thomas (28) developed a chlorination-ethanolamine holocellulose preparation procedure which was modified by Wethern (29). This modified procedure was used to prepare a holocellulose for comparison with chlorite holocellulose as to resistant xylan. Wethern's work indicated that his modified procedure produced hemicelluloses of higher degree of polymerization than those from chlorite holocellulose. The procedure consisted essentially of the following steps: (1) Chlorination of cold, moist wood meal with chlorine dissolved in carbon tetrachloride at -5 to -10°C. for five minutes, (2) two washes with hot 3% ethanolamine in alcohol, (3) two three-minute soaks in the hot 3% ethanolamine wash, (4) a wash with cool 95% alcohol and finally with ice water, (5) Steps 1-4 repeated, and (6) thorough washing of the final product with water and acetone, followed by air drying.

ASPEN CHLORITE PULP PREPARATION

During the course of experimentation a small-scale pulping procedure was developed for the production of pulps high in resistant xylan content from aspen chips or shavings. It consisted of an alkaline

pretreatment followed by delignification with acidified sodium chlorite at room temperature. For lack of a better name all pulps prepared by this process or modifications thereof were called "aspen chlorite pulps" to distinguish them from aspen kraft pulp, aspen sulfite pulp, etc. The standard procedures adopted for the preparation of aspen chlorite pulps from wood chips and wood shavings are given below. Deviations from these so-called standard procedures will be emphasized in the discussion of results. Unless different experimental conditions are specified, it is to be understood that the following procedures were used.

Chlorite Pulp from Aspen Chips

One-hundred grams of air-dried chips of known moisture content were soaked in 1000 ml. of 17.5% sodium hydroxide with occasional stirring for 24 hours. The thoroughly penetrated chips were then filtered in a Buchner funnel on a 150-mesh stainless steel wire screen, washed externally with water, soaked in fresh distilled water for one hour, and filtered again. The chips were next acidified by soaking in 3000 ml. of 5% acetic acid for four hours, filtered, washed externally, and transferred to a 4-liter beaker containing 2000 ml. of distilled water. Delignification was carried out by adding 50 ml. of glacial acetic acid and 100 grams of technical-grade sodium chlorite, and allowing the reaction to take place for 48 hours at room temperature. The beaker was kept covered with a watch glass in a well-ventilated hood, and the contents were stirred occasionally during the reaction period. The 48-hour period was found to be sufficiently long for good softening of alkaline-pretreated chips. When no pretreatment was given, no appreciable softening of the chips occurred within a chloriting period of one to two weeks. Alkaline pretreatment

therefore greatly increased the rate of penetration of the chlorite liquor into the chips and also may have removed some fiber-bonding material of an unknown nature.

At the end of the delignification period, the acidified sodium chlorite liquor was removed by filtration, using the stainless steel wire. This filtration was carried out in a hood, and the chips were washed externally several times before they were removed from the hood. The partially washed chips were then converted to a pulp by passage through a small laboratory Bauer refiner or by batchwise stirring in a British disintegrator if they were very soft. After the disintegration process the pulp fibers were recovered by filtration on the fine stainless steel screen, washed thoroughly with distilled water, given a final acetone wash, and air dried. The airdry pulp was stored in a tightly sealed bottle from which samples were removed for moisture, pentosan, and alpha-cellulose analyses.

Chlorite Pulp from Aspen Shavings

Aspen shavings were converted to chlorite pulps by a procedure similar to the one just described. For 50 grams of airdry shavings the following procedure and proportions of chemicals were used. The shavings were treated with 1000 ml. of 17.5% sodium hydroxide for four hours. They were then filtered on the stainless steel screen in a Buchner funnel, washed with water, washed and soaked in 5% acetic acid for several minutes, and again washed with water. The treated shavings were then transferred to a 2-liter beaker which contained 1200 ml. of distilled water, and to this were added 25 ml. of glacial acetic acid and 30 grams of sodium chlorite.

The reaction was allowed to proceed for 24 hours at room temperature with occasional stirring. A 24-hour period was found sufficient for the delignification of shavings and wood meal which were not dried between alkaline treatment and chlorite treatment, whereas 48 hours were required for the chips.

After the 24-hour reaction period was completed, the shavings were filtered, washed, disintegrated or defibered in the small Bauer or the British disintegrator, and the pulp fibers were collected by filtration, washed thoroughly with water and acetone, and air dried.

"Chlorite Pulping" of Wood Meal

Aspenwood meal was chlorited at room temperature after alkaline pretreatment for the purpose of comparing the resistant xylan contents of the products obtained from shavings and wood meal. The treatment was similar to that just described for shavings, except that the pulping or disintegration process in the Bauer was eliminated. The alkaline pretreatment was varied to determine the effect of alkali concentration and length of treatment, but the room-temperature sodium chlorite treatment was identical to that used for shavings.

CHLORITE TREATMENT AT ROOM TEMPERATURE
WITHOUT ALKALINE PRETREATMENT

Chips, shavings, and wood meal were treated directly with acidified sodium chlorite at room temperature without the alkaline pretreatment. The proportions of wood, water, and chemicals used for each material were identical with those used for the second stage of the chlorite pulping procedure for the corresponding materials. However, a

much longer reaction time was required to obtain a substantial yield reduction. Such differences in treatment will be brought forth in the discussion of results.

PRESENTATION AND DISCUSSION OF DATA

The data on the following pages are presented in nine main sections, and each section will contain a discussion of the data included in it. The sections are arranged in much the same chronological order as the laboratory work. This arrangement should assist the reader in following the experimental attack on the problem.

PRELIMINARY INVESTIGATIONS

VERIFICATION OF MARCH'S DATA

As stated previously, March found that an alpha-cellulose prepared from bleached aspen kraft pulp contained 8.9% xylan, but one prepared from aspen chlorite holocellulose contained only 1.2% xylan. March's experiments were repeated on the new sample of aspenwood. Kraft cook 1 was carried out on 600 grams of aspen chips according to the cooking conditions employed by March. A summary of this cook may be found in Table I of the appendix. The unbleached pulp yield was 53.7% of the ovendry wood. A 30-gram sample of the unbleached pulp was bleached using the mild conditions of March. This consisted of a one-hour bleach at 60°C., using 7% sodium chlorite based on the pulp (600 ml. of water, 3 ml. of acetic acid, and 2 grams of sodium chlorite).

Chlorite holocellulose was prepared from 50 grams of the air-dried, unextracted, 30-50 mesh aspenwood meal by the standard procedure. The approximate yield was 82% of the unextracted wood.

Four alpha-celluloses were then prepared, one each from the bleached

pulp and the holocellulose under nitrogen, and one from each in the air according to the standard procedure (Institute Method 421), using 17.5% sodium hydroxide for all extractions. The extractions under nitrogen were carried out in suction flasks fitted with two stopcocks, one for the admission of nitrogen and one for the introduction of alkali. The material to be extracted was placed in a flask, which was then evacuated and filled with oxygen-free nitrogen three times. The alkali was then added by connecting a dropping funnel to the stopcock with a very short piece of rubber tubing and allowing the alkali to flow in and displace its volume of nitrogen. After the alkali was added, the flask was swirled for good mixing of the contents and given a final evacuation and refilling with nitrogen. These extractions were carried out for two hours at 20°C., after which the products were filtered and washed in the same manner as for the standard extraction procedure.

The four alpha-celluloses were next analyzed for xylan. The two prepared by the standard procedure were analyzed by the gravimetric phloroglucinol procedure (Institute Method 23), the procedure used by March. Those prepared under nitrogen were analyzed by the volumetric bromate-bromide procedure (Institute Method 23a). The results of this work are presented in Table II.

TABLE II

COMPARISON OF METHODS OF ALPHA-CELLULOSE PREPARATION AND XYLAN ANALYSIS

	Resistant Xylan Contents of Alpha-Celluloses, %	
	From Chlorite Holocellulose	From Bleached Kraft Pulp
March's data	1.2	8.9
Author's data, March's procedure	2.3	8.5
Author's data, procedure B (nitrogen, volumetric xylan)	2.4	7.8

LARGE-SCALE PREPARATION OF ALPHA-CELLULOSES

The preparation of the chlorite holocellulose and alpha-cellulose from the 30-50 mesh wood meal used for the kraft cooks was described in the section on Experimental Procedures. This alpha-cellulose was prepared by extraction with 10% potassium hydroxide in an open beaker and was air dried instead of being oven dried.

The large-scale preparation of the bleached kraft pulp was carried out in two batches, one of 100 grams and a second of 160 grams, using the same conditions as for the small-scale bleach (7% sodium chlorite, one hour, 60°C.). The ovendry yield was 98.0% based on the unbleached pulp. The bleached pulp was then extracted with 17.5% sodium hydroxide by the standard procedure. After filtering and washing, this alpha-cellulose was air dried.

Samples of these two alpha-celluloses were analyzed for xylan by the standard volumetric procedure. The data may be found in Table III.

TABLE III

RESULTS OF LARGE-SCALE ALPHA-CELLULOSE PREPARATIONS

	Alpha-Cellulose From	
	Chlorite Holocellulose	Bleached Kraft Pulp
Yield of material extracted, % (based on orig. wood)[1]	65.0	52.6
Xylan content of material extracted, %	21.6	16.2
Alpha-cellulose content, % (based on material extracted)	61.0	87.7
Alpha-cellulose yield, % (based on original wood)	51.8	46.2
Resistant xylan content, %	2.0	8.1
Resistant xylan content, % (based on original wood)	1.0	3.7

[1] In this and all succeeding tables all yield data based on the original wood refer to the unextracted, ovendry basis.

It can be seen from the xylan contents of the alpha-celluloses of Table II and Table III that March's data have been qualitatively corroborated. Although the magnitude of the difference in alkali-resistant xylan was not quite as great as that obtained by March, the effect was definitely shown to be a real one.

The data showed no marked differences between the results of the methods used, so it was decided to adopt the following as standard procedures for determining resistant xylan: (1) Institute Method 421 for alpha-cellulose and (2) Institute Method 23a for the volumetric analysis of xylan. These are the methods given as Standard Procedures in the section on Experimental Procedures.

HYDROLYSIS OF ALPHA-CELLULOSES

The data of the preceding section show that an alpha-cellulose from a bleached kraft pulp gives more furfural on distillation with 12% hydrochloric acid than does one from chlorite holocellulose. The furfural produced is calculated as xylan. Therefore, it cannot definitely be stated that the greater amount of furfural produced from the kraft pulp alpha-cellulose actually is caused by a greater amount of xylan in that alpha-cellulose. However, this can be established by hydrolysis of the alpha-celluloses to simple sugars and identification of these sugars by means of paper partition chromatography.

Samples of the two alpha-celluloses from chlorite holocellulose (containing 2.3 and 2.4% xylan) and of the two from the bleached kraft pulp (containing 8.5 and 7.8% xylan) were hydrolyzed, neutralized, and concentrated by the standard procedure. In each case 4.0 grams of alpha-cellulose were hydrolyzed and the final sirups were adjusted to equal volumes. These sirups were spotted on Schleicher and Schuell No. 598YD and on Whatman No. 1 filter paper strips and chromatographed with butanol-ethanol-water as the developer. The results of this work were as follows: (1) each of the sirups from the alpha-celluloses from chlorite holocellulose produced a heavy glucose spot and a very faint xylose spot, and (2) each of the sirups from the kraft pulp alpha-celluloses produced a heavy glucose spot plus a fairly heavy xylose spot.

These experiments qualitatively, but definitely, established that the higher furfural yield from the kraft pulp alpha-cellulose was actually due to a higher xylan content in that alpha-cellulose.

OVERBLEACHING OF KRAFT PULP AND KRAFT PULP ALPHA-CELLULOSE

In order to determine whether the strong chloriting conditions of the holocellulose procedure may be responsible for its low-resistant xylan content, samples of the unbleached kraft pulp and of the kraft alpha-cellulose from the large-scale preparation were overbleached. The kraft pulp was given a two-hour bleach by the standard chlorite holocellulose procedure, and the kraft alpha-cellulose was given a one-hour bleach by the same procedure. These two bleached products and a second sample of the kraft alpha-cellulose were then extracted with 17.5% sodium hydroxide by the standard procedure, and the xylan contents of the bleached products and of the three alpha-celluloses were determined. These results are presented in Table IV.

TABLE IV

EFFECT OF OVERBLEACHING AND RE-EXTRACTION ON RESISTANT XYLAN

	Alpha-Celluloses From		
	Overbleached Kraft Pulp	Kraft Alpha-Cellulose	Overbleached Kraft Alpha-Cellulose
Xylan content before bleaching, %	16.1	8.1	8.1
Number and hours of chlorite treatments	2	0	1
Bleaching yield, %	98.2	--	98.2
Xylan content after bleaching, %	16.4	--	8.0
Alpha-cellulose content, % (based on material extracted)	87.8	97.6	97.8
Alpha-cellulose yield, % (based on original wood)	45.4	45.1	44.4
Resistant xylan content, %	8.1	6.9	5.9

Obviously the strong bleaching conditions have no specific effect on resistant xylan content. Mild bleaching and very strong bleaching both produced alpha-celluloses with 8.1% resistant xylan. It is also important to note that, although bleaching the alpha-cellulose prior to a second alkaline extraction slightly decreases the resistant xylan content from that obtained without bleaching, neither value (5.9% or 6.9%) approaches the low values obtained for alpha-celluloses from chlorite holocellulose (2.0-2.4%). Apparently strong sodium chlorite treatment does not exert an appreciable degrading influence on the alkali-resistant xylan in the kraft pulp. Whether it does or does not degrade the xylan in the original wood during the chlorite holocellulose preparation cannot be decided from this work.

MODIFIED THOMAS HOLOCELLULOSE

The preparation of this holocellulose was described under Special Procedures. The alpha-cellulose was prepared by the standard 17.5% sodium hydroxide extraction procedure. The reason for investigating a second method of holocellulose preparation was to attempt to determine whether it is the strong sodium chlorite treatment which is responsible for the low-resistant xylan content of aspen chlorite holocellulose. The data are shown in Table V.

TABLE V

ALPHA-CELLULOSE FROM THOMAS HOLOCELLULOSE

Holocellulose yield, %	86.7
Xylan content of holocellulose, %	21.3
Alpha-cellulose content, % (based on holocellulose)	59.0
Alpha-cellulose yield, % (based on original wood)	51.7
Resistant xylan content, %	4.8
Resistant xylan content, % (based on original wood)	2.5

It was concluded from this work that the chlorite holocellulose procedure may be somewhat more degrading in its action on xylan than the modified Thomas holocellulose procedure. Wethern (29) obtained much more substantial proof of this by determining the viscosities of the hemicelluloses extracted from the two types of holocellulose.

However, degradation caused by sodium chlorite treatment cannot be the entire explanation to the difference in xylan content of a kraft pulp alpha-cellulose and one from chlorite holocellulose, because the former also has more resistant xylan than the alpha-cellulose from Thomas holocellulose.

INVESTIGATION OF THE EFFECT OF VARIOUS COOKING PROCEDURES ON RESISTANT XYLAN

KRAFT COOKS ON HOLOCELLULOSE, ALPHA-CELLULOSE, AND COTTON LINTERS

Kraft cooks 2, 3, and 4 were carried out on 200 grams each of the chlorite holocellulose, alpha-cellulose therefrom, and cotton linters, respectively. The purpose of the cook on holocellulose was to determine

the effect of the kraft conditions on the xylan as it exists in the holocellulose. Alpha-cellulose and cotton linters were cooked to eliminate from consideration the vague possibility that cellulose could be converted to resistant xylan under the conditions of a kraft digestion. The cooked holocellulose was analyzed for alpha-cellulose and resistant xylan. The cooked alpha-cellulose and cotton linters were analyzed directly for xylan. The "xylan" values shown for cotton linters are those actually obtained by titration and not the corrected values. A direct comparison with the other values can be made by considering the cotton linters values equal to zero. These data are given in Table VI. The cooking conditions used may be found in Table II of the Appendix.

TABLE VI

RESULTS OF KRAFT COOKS 2, 3, AND 4

	Material Cooked		
	Holocellulose	Alpha-Cellulose	Cotton Linters
Yield of product, % (based on material cooked)	61.9	82.3	86.0
Yield of material cooked, % (based on orig. wood)	85.0	51.8	--
Yield of product, % (based on orig. wood)	52.6	42.6	--
Xylan content of material cooked, %	21.6	2.0	0.8
Xylan content of product, %	17.8	1.0	0.4
Alpha-cellulose content, % (based on product)	77.2	--	97.3
Alpha-cellulose yield, % (based on orig. wood)	40.6	--	--
Resistant xylan content, %	1.6	--	--

The most important data of this table are the xylan contents of the products. Neither alpha-cellulose nor cotton linters showed an increase in xylan content after exposure to the kraft cooking conditions. This establishes the fact that resistant xylan is not generated from cellulose during a kraft cook.

Although the xylan content of the kraft-cooked holocellulose was slightly higher than of a normal pulp, the alpha extraction showed most of it to be alkali soluble. Therefore a kraft cook does not increase the alkaline resistance of xylan as it exists in chlorite holocellulose.

It is interesting to note the similarity in yield and xylan content of the kraft-cooked holocellulose and the bleached kraft pulp. However, this similarity no longer exists in the alpha-celluloses prepared from these two products. This comparison is made in Table VII.

TABLE VII

COMPARISON OF KRAFT COOKS ON WOOD AND HOLOCELLULOSE

	Bleached Kraft Pulp	Kraft-Cooked Holocellulose
Pulp yield, % (based on original wood)	52.6	52.6
Xylan content of pulp, %	16.2	17.8
Alpha-cellulose content, %	87.7	77.2
Resistant xylan content, %	8.1	1.6

The xylan content of the kraft-cooked holocellulose was 17.8%, whereas that of the alpha-cellulose produced by direct extraction of the holocellulose with 17.5% sodium hydroxide was only 2.0% (see Table III).

thus it can be seen that a kraft cook is much less specific in its removal of xylan than is cold concentrated alkali. However, the yield of 52.6% is very close to the alpha-cellulose yield of 51.8%. Therefore the hot alkaline cook must remove more non-xylan than the concentrated alkali. This is in agreement with the statement of Preece (30) that hot alkaline extraction of woods favors the dissolution of non-pentosan, whereas cold extraction favors the dissolution of xylan.

In spite of the lower lignin content of the holocellulose before cooking, there is not a great difference in the xylan contents of the pulps. Apparently the presence of lignin is not required to protect the xylan from dissolution. However, the much lower alpha-cellulose content of the kraft-cooked holocellulose indicates that the absence of lignin during cooking may be responsible for a greater degradation of the non-xylan fraction.

SODA AND SULFITE COOKS ON ASPEN CHIPS

The soda cook was carried out with 24% active alkali as sodium hydroxide by the same procedure as the kraft cook except that the cooking time was increased by about one hour with the intent of obtaining approximately the same yield. The increased time was thought necessary because the rate of delignification is usually slower for a soda cook than for a kraft cook.

The sulfite cook was made with a sodium-base liquor containing 1.5% combined and 5% free sulfur dioxide. The liquor was poured over the chips, the digester sealed, and penetration allowed to take place overnight at room temperature. Because of this penetration period it was decided that

a 7.6-hour cook would be of sufficient length to give a pulp yield in the range of that obtained for the kraft cook. The alpha-celluloses were prepared by the standard procedure after mild bleaching of the pulps with sodium chlorite. The results of these cooks are tabulated in Table VIII in comparison with kraft Cook 1, and the cooking conditions are given in Table I of the Appendix.

TABLE VIII

COMPARISON OF KRAFT, SODA, AND SULFITE PULPS

	Kraft 1	Soda	Sulfite
Unscreened pulp yield, %	53.7	50.9	51.6
Permanganate number of pulp	8.1	6.7	3.2
Xylan content of unbleached pulp, %	16.1	14.1	5.5
Yield on bleaching, %	98.0	97.2	96.0
Xylan content of bleached pulp, %	16.2	14.1	5.5
Alpha-cellulose content, % (based on bleached pulp)	87.7	88.2	85.5
Alpha-cellulose yield, % (based on original wood)	46.2	43.6	43.2
Resistant xylan content, %	8.1	7.7	0.2

There is very little difference in the xylan content of the alpha-celluloses produced from kraft and soda pulp. As it turned out, the soda cook was more drastic than the kraft cook. If the kraft pulp yield of 53.7% had been more closely approached in the soda cook, the alpha-cellulose yield and xylan content might well have been closer to the kraft pulp values. On the other hand, the sulfite pulp contains less alpha-cellulose, less total xylan, and considerably less resistant xylan than the alkaline-cooked pulps. This behavior has, of course, been known for a long time in the dissolving pulp industry, but an actual laboratory comparison of kraft and soda vs. sulfite pulps produced in

comparable yields from the same wood was nevertheless of considerable value in this work. It is obvious from the data that the effect is one of alkalinity vs. acidity; the xylan is very readily attacked by acidic cooking liquor and not nearly as much by the alkaline liquors.

Jayme and Koppen (31) have investigated the differences between sulfate and sulfite pulps. According to them sulfate pulps show much less acidic character than sulfite pulps as measured by ion-binding capacity and uronic anhydride content. They state that in alkaline pulping larger proportions of polyuronides are removed which resist acidic pulping, and the higher solubility of the hemicellulose portion of the sulfite pulp in sodium hydroxide solution depends not only on lower D.P. but also on the presence of carboxyl groups. They reason that it is not necessary to assume that all of the carbon dioxide comes from pure polyuronide, since it is also possible that the polyuronide-carboxyl groups are distributed over the hemicellulose chains. In this case a uronic acid anhydride unit attached to the hemicellulose molecule could impart a higher solubility in alkalies than would exist for a comparable molecule without the acid group.

SULFITE COOK ON COTTON LINTERS

Referring to Table VIII, it can be seen that the soda and sulfite pulps were produced in approximately equal yields and with very low lignin contents as shown by the permanganate numbers. However, the soda pulp has 14.1% xylan, whereas the sulfite pulp has 5.5% xylan. If the sulfite pulp is 8.6% lower in xylan content, it must then be approximately 8.6% higher in some other component or components. The major portion of these other

components must be either cellulose or hemicellulose made up of anhydroglucose chains. This rough calculation indicates that the sulfite process, while removing much more xylan, allows more of the cellulose or "glucans" to remain in the pulp than does an alkaline process. An alkaline process therefore seems to have a general degrading and dissolving action on the entire carbohydrate fraction, whereas the sulfite process is more specific to the readily hydrolyzable xylan.

If this is so, a sulfite cook on cotton linters should produce a material in higher yield than that obtained from the kraft cook on cotton linters. This sulfite cook was carried out with the use of 1.5% combined and 5% free sulfur dioxide and a 10:1 water-to-cotton ratio. A 5.5-hour cook was used instead of the 6.5-hour cook used for aspen chips because the long penetration period was not required. The results are shown in Table IX in comparison with the kraft cook on cotton linters. The cooking conditions of the sulfite cook may be found in Table III of the Appendix.

TABLE IX

KRAFT AND SULFITE COOKS ON COTTON LINTERS

	Kraft	Sulfite
Alpha-cellulose content of starting material, %	99.3	99.3
Yield of product, %	86.0	97.0
Visual form of product	Fibrous and fluffy	Powder
Alpha-cellulose content of product, %	97.3	82.4

Admittedly the conditions of both cooks were more drastic than those on the aspen chips because no lignin was present to exert a protective action or to consume chemicals. Nevertheless, the kraft cook product was almost identical with the original cotton linters and had a very high alpha-cellulose content, whereas the product of the sulfite cook, a hydrocellulose, although extremely degraded, was obtained in the high yield of 97%.

These data support the contention that the sulfite cook on aspen chips (Table VIII) permitted a larger portion of the non-pentosan alpha-cellulose of the wood to remain in the pulp at the expense of the readily hydrolyzed hemicelluloses than did the soda or kraft cooks. This does not mean that the alpha-cellulose was less degraded by the sulfite cook. Hydrolysis of the alpha-cellulose no doubt occurred as evidenced by the lower analytical alpha-cellulose content of the sulfite pulp. Thus it would seem that the sulfite cook produces "hemicelluloses", whereas the alkaline cooks allow a larger part of the original hemicelluloses to remain in the pulp at the expense of some of the original alpha-cellulose.

KRAFT COOKS 5 AND 6

The effects of prolonging the kraft cooking time (kraft Cook 5) and of semichemical kraft cooking (kraft Cook 6) were determined and the data compared with kraft Cook 1. For Cook 5 the active alkali was maintained at 24%, and the cooking time increased by 45 minutes. For Cook 6 the active alkali was reduced to 15%, and the cooking time reduced by 45 minutes. The pulps were bleached by the standard procedure. The results

are presented in Table X. The cooking conditions may be found in Table IV of the Appendix.

TABLE X

EFFECT OF COOKING CONDITIONS ON RESISTANT XYLAN

	Semichemical Pulp	Kraft Pulp (Kraft Cook 1)	Kraft Pulp (Kraft Cook 5)
Cooking time, min.	60	105	150
Unbleached pulp yield, %	66.0	53.7	52.8
Permanganate number	34.9	8.1	7.2
Xylan content of unbleached pulp, %	16.4	16.1	15.9
Yield on bleaching, %	86.3	96.2	95.6
Alpha content, % (based on bleached pulp)	80.7	87.8	89.8
Alpha yield, % (based on original wood)	46.0	45.4	45.4
Resistant xylan content, %	4.3	8.1	8.6

It is unfortunate that the additional 45 minutes employed for Cook 5 did not greatly reduce the yield or permanganate number. As it was, the additional time in contact with the cooking liquor produced very little change in the results as compared with Cook 1. The slight increase in resistant xylan content is within experimental error. A more valuable comparison could have been made by producing a kraft pulp with a yield midway between that of the semichemical and that of the soft kraft pulp, e.g., 59-60%. Time did not permit this, however.

The experiments on the semichemical pulp established the fact that an alpha-cellulose from a bleached semichemical kraft pulp retained only about one half as much resistant xylan as did one from a chemical pulp. Whether this can be attributed to the higher lignin content of the semichemical pulp or to the shorter time in contact with alkali, cannot be said.

SODIUM CHLORITE DELIGNIFICATION OF ASPEN CHIPS

ASPEN CHLORITE PULP NO. 1

Cold alkaline pretreatment of aspen chips followed by delignification with a large excess of acidified sodium chlorite at room temperature was found to produce pulps with a high resistant xylan content. This xylan was also shown to be very resistant to overbleaching and to a second alpha extraction. Thus these pulps apparently have the same characteristics as alkaline-cooked pulps with respect to resistant xylan.

Chlorite pulp 1 was prepared according to the procedure described in the section on Special Procedures. One sample of this pulp was extracted directly with 17.5% sodium hydroxide by the standard procedure. This material was called "alpha-cellulose" because its high yield indicated that it was not a true alpha-cellulose. A second sample was bleached for one hour by the standard procedure prior to the alpha-cellulose preparation.

The "alpha-cellulose" from the unbleached pulp was itself bleached by the same procedure and re-extracted with 17.5% sodium hydroxide to determine the resistance of the xylan to this drastic treatment. The data of these experiments are presented in Tables XI and XII.

TABLE XI

RESULTS OF COLD CHLORITE DELIGNIFICATION OF ALKALINE-TREATED CHIPS

Unbleached pulp yield, %	70.1
Permanganate number	6.0
Xylan content of unbleached pulp, %	20.0
Bleaching yield, %	91.7
Bleached pulp yield, %	64.3
Alpha-cellulose content, % (based on bleached pulp)	84.6
Alpha-cellulose yield, % (based on original wood)	54.4
Resistant xylan content, %	10.9

TABLE XII

RESULTS OF BLEACHING AND RE-EXTRACTION OF "ALPHA-CELLULOSE" FROM UNBLEACHED CHLORITE PULP

Unbleached pulp yield, %	70.1
"Alpha-cellulose" content, % (based on unbleached pulp)	82.6
"Alpha-cellulose" yield, % (based on original wood)	57.8
Xylan content of "alpha-cellulose", %	13.8
Alpha-cellulose content, % (based on "alpha-cellulose")	87.7
Alpha-cellulose yield, % (based on original wood)	50.7
Resistant xylan content, %	9.5

Even after a full hour bleach of the pulp by the chlorite holocellulose procedure, the alpha-cellulose yield was still 54.4% of the original wood, and the xylan content was 10.9%. This is higher than the results obtained for the chemical kraft pulps, but the reason for the high xylan content is undoubtedly similar. The resistance of this xylan to bleaching and re-extraction with 17.5% sodium hydroxide is shown in Table XII. The xylan content after a second alpha extraction was 9.5%, a value approaching those obtained for the alpha-celluloses

from the kraft pulps. However, the alpha-cellulose yield was 50.7%, as compared with only 45.4% for the kraft pulps. Thus, while "producing" resistant xylan, this chlorite pulping procedure causes much less degradation of the cellulose fraction.

This method of pulping provides a simpler experimental method of studying the phenomenon of resistant xylan than the standard kraft pulping procedure. Since an alkaline treatment is also used in this method prior to chloriting, the possibility exists that alkaline treatment is responsible for the resistance of the xylan to subsequent alkaline extraction. It may also be due to some difference between wood chips and wood meal, because again when working with chips, the high-xylan content alpha-celluloses have been encountered. The fact that the sodium chlorite treatment was carried out in the cold may also be important. Less degradation of the xylan may be the result of such a treatment.

DIRECT ROOM-TEMPERATURE CHLORITE DELIGNIFICATION OF WOOD CHIPS

The alkaline treatment of the chips was eliminated; only an overnight soak in distilled water was used. The same amounts of chips, water, acetic acid, and sodium chlorite were used as for the experiment described in the preceding section. After standing for six days the chips became lighter in color, but they were still very hard. The liquor was filtered off, and a second charge of water and chemicals added. After seven additional days at room temperature, the chips were white but definitely not at all softened, and hence no attempt was made to defiber them in the Bauer refiner. Instead they were washed, soaked for several days in frequent changes of distilled water, and finally air dried. After

yield and moisture determinations the dry chips were converted to 30-60 mesh meal in a Wiley mill.

One portion of this holocellulose was converted directly to alpha-cellulose, whereas a second portion was bleached for one hour by the standard holocellulose procedure and then converted to alpha-cellulose by the standard procedure. The results of the work are contained in Table XIII.

TABLE XIII

RESULTS OF DIRECT COLD CHLORITE DELIGNIFICATION OF CHIPS

	Original Product	Bleached Product After Hot Chloriting
Holocellulose yield, %	86.8	83.1
Alpha-cellulose yield, % (based on original wood)	51.8	50.8
Resistant xylan content, %	5.9	4.7

It is significant to note the great difference in reaction rate between chlorine dioxide and the untreated and the alkaline-treated chips. After alkaline treatment the chips were well pulped in two days, whereas the untreated chips were not pulped even after 13 days. The results of Table XIII should be compared with those of Table XI. The resistant xylan contents of the original product and the hot chlorited product from the alkaline treated chips were 13.8 and 10.9% as compared with 5.9 and 4.7% for the untreated chips. These data indicate that alkaline treatment is important in speeding up the rate of delignification and in protecting the xylan from degradation.

Even though considerably lower than from alkaline-treated chips, the xylan contents of 5.9 and 4.7% in alpha-celluloses from cold chlorited chips were higher than the 2% range obtained from hot chlorited wood meal. Again the possibility is suggested that hot acidified sodium chlorite treatment or the use of wood meal (or both) might promote the removal of xylan.

HOT CHLORITE DELIGNIFICATION OF WOOD CHIPS

Room-temperature sodium chlorite delignification of aspen chips showed that 17.5% sodium hydroxide pretreatment followed by the chlorite treatment produced a pulp with a large amount of resistant xylan, but that direct chlorite treatment was an extremely slow reaction, the chips could not be pulped, and the material produced was fairly low in alkali-resistant xylan. A measure of the relative effects of alkaline treatment and temperature of the chlorite treatment was obtained by repeating the previous experiments using the hot chlorite procedure instead of the cold procedure.

Chlorite pulp 2 was prepared as follows: 100 grams of chips were treated with 17.5% sodium hydroxide by the standard procedure, washed, and then delignified by a four-hour treatment with sodium chlorite at 70-80°C. using the standard procedure. The mixture was then allowed to cool to room temperature before filtering, pulping, and washing. A sample of the airdry pulp was then converted to alpha-cellulose and resistant xylan determined. The data are shown in Table XIV.

TABLE XIV

RESULTS OF HOT CHLORITE DELIGNIFICATION OF ALKALINE-TREATED CHIPS

Pulp yield, %	65.4
Xylan content of pulp, %	19.7
Alpha-cellulose content, % (based on the pulp)	79.6
Alpha-cellulose content, % (based on original wood)	52.1
Resistant xylan content, %	9.2

The sequence of the preceding experiment was reversed to demonstrate conclusively that alkaline treatment prior to any other treatment is the important factor in the "production" of alkali-resistant xylan. Small aspen chips were used to promote penetration of the hot chlorite liquor. One hundred grams of the small chips were soaked overnight in water and then chlorited at 70-80°C. However, the third and fourth additions of sodium chlorite were allowed two hours' reaction time since penetration was slow. After cooling to room temperature, the chips were filtered, diffused in water for three hours, filtered, and extracted with 1000 ml. of 17.5% sodium hydroxide for 10 hours. The product was then filtered, washed, and pulped by the usual procedure. The yield of pulp was 48.6% and was therefore already an alpha pulp. The xylan content of this pulp was found to be 3.7%.

These data, together with those previously obtained for cold chlorite treatment, show that alkaline treatment prior to chloriting is required to produce alkali-resistant xylan. Hot chloriting may cause a certain amount of degradation and/or oxidation not encountered in cold

chloriting, since the xylan contents were lower in alpha-celluloses prepared after hot treatment as compared to parallel experiments using cold treatment. However, the temperature of chloriting is of minor importance as compared to alkaline treatment.

INVESTIGATION OF WOOD MEAL

CHLORITE PULPING PROCEDURE APPLIED TO WOOD MEAL

After discovering the great difference in resistant xylan content between the products of cold chloriting of alkaline-treated vs. untreated wood chips, the next step was to repeat the experiments using wood meal. If the resistant xylan were "produced" by some chemical reaction during alkaline pretreatment, the same chemical reaction should take place on treatment of wood meal with alkali.

A batch of 40-60 mesh wood meal was extracted with 17.5% sodium hydroxide for four hours at room temperature. After filtering and washing, the material was air dried for a yield determination. The yield of alkaline-extracted meal was 78.6% with a xylan content of 11.7%. It was then treated with sodium chlorite at room temperature by the usual procedure except that separate batches were allowed reaction periods of two, four, and six days. The results are presented in Table XV.

TABLE XV

CHLORITE PULPING OF WOOD MEAL

Reaction time	2 Days	4 Days	6 Days
Yield on alkaline extraction, %	78.6	78.6	78.6
"Pulp" yield, % (based on extracted meal)	80.5	75.8	75.5
"Pulp" yield, % (based on original wood)	63.2	59.6	59.3
Alpha-cellulose content, % (based on "pulp")	80.2	82.0	82.6
Alpha-cellulose yield, % (based on original wood)	50.8	48.9	48.9
Resistant xylan content, %	5.1	4.0	3.8

Four days were required for complete reaction as indicated by the "pulp" yields. However, a two-day reaction period produced sufficient delignification to give an alpha-cellulose yield nearly equivalent to the analytically determined alpha-cellulose content of the aspenwood. This is the same reaction time as was found to be satisfactory for alkaline-treated chips. However, the resistant xylan content of 5.1% is much lower than that of 10.9% xylan obtained for the alpha-cellulose from chlorite pulping of chips. The fact that extending the chlorite treatment to four and six days further reduced the resistant xylan content showed that even the 5.1% was not all truly resistant xylan.

This work shows that the entire cause of resistant xylan cannot be attributed to a chemical reaction during alkaline pretreatment or alkaline pulping of chips. The cause appears to be more related to a difference between wood chips and wood meal. This could be either an increase in physical availability of the xylan to alkaline extraction or a chemical degradation of the xylan caused by grinding of the wood meal.

DIRECT ROOM-TEMPERATURE CHLORITE TREATMENT OF WOOD MEAL

Three samples of the wood meal were treated directly with acidified sodium chlorite at room temperature for two, four, and six days. The identical procedures were used as for the work of the preceding section, except that the alkaline pretreatment of the meal was eliminated. The two-day product was not converted to alpha-cellulose because of the high yield. The data are shown in Table XVI.

TABLE XVI

ROOM-TEMPERATURE CHLORITE TREATMENT OF WOOD MEAL

Reaction time	2 Days	4 Days	6 Days
Holocellulose yield, %	90.4	87.2	85.2
Alpha-cellulose content, % (based on holocellulose)	--	58.6	55.9
Alpha-cellulose yield, % (based on original wood)	--	51.1	51.0
Resistant xylan content, %	--	4.3	4.2

These resistant xylan values are almost identical with those obtained after alkaline treatment (Table XV). Thus it has been established that alkaline pretreatment has very little effect on the resistant xylan content of wood meal.

The fact that resistant xylan contents of 4.2 and 4.3% were obtained after room-temperature chlorite treatment as compared to 2.0 to 2.4% obtained after hot chlorite treatment of wood meal indicates that the high-temperature treatment either causes greater degradation of the xylan or increases the physical availability of the xylan.

The reaction rate between sodium chlorite and lignin is much more rapid with an alkaline pretreatment than without one. This was shown to be true for chips as well as wood meal. The reaction of sodium chlorite with alkaline-treated wood meal was complete in four days. However, the reaction of sodium chlorite with untreated meal was not complete even after six days. This can be seen by an examination of the "pulp" yield and holocellulose yield data of Tables XV and XVI. Alkaline pretreatment probably increases the physical availability of the lignin to the active oxidizing agent. Thus, by means of its swelling and dissolving action, the alkali increases the number and size of capillaries available for penetration of the oxidizing agent into the fine structure of the wood.

However, the possibility cannot be overlooked that alkaline pretreatment may also cause a chemical modification of the lignin-carbohydrate system, and in so doing increases the chemical reactivity of the lignin toward sodium chlorite.

EFFECT OF CONCENTRATION OF ALKALI DURING PRETREATMENT AND MESH SIZE OF WOOD MEAL ON RESISTANT XYLAN

A series of experiments was carried out on 40-60 mesh wood meal to determine the effect of concentration of alkali and time of pretreatment on the resistant xylan. The usual procedure was used, consisting of an alkaline soak followed by sodium chlorite treatment at room temperature for 24 hours. Alpha-celluloses were then prepared from the airdry "pulps" by the standard procedure. The data are presented in Table XVII.

TABLE XVII

EFFECT OF VARIOUS PRETREATMENTS ON RESISTANT XYLAN

Pretreatment	1	2	3	4
NaOH concentration, %	4	8	8	12
Time, hours	4	4	20	4
"Pulp" yield, %	65.7	63.4	61.9	62.1
Alpha-cellulose content (based on pulp), %	78.3	80.5	79.8	82.6
Alpha-cellulose yield, % (based on original wood)	51.4	51.1	49.4	51.3
Resistant xylan content, %	6.0	5.6	2.6	6.2

Using pretreatment 2, a coarsely ground meal (10-30 mesh) and a finely ground meal (60-80 mesh) were next investigated. The same conditions of chlorite treatment and alpha-cellulose preparation were used, and the results are given in Table XVIII.

TABLE XVIII

EFFECT OF MESH SIZE OF WOOD MEAL ON RESISTANT XYLAN

Mesh Size	Coarse (10-30 mesh)	Medium (40-60 mesh)	Fine (60-80 mesh)
Pretreatment	2	2	2
"Pulp" yield, %	67.8	63.4	65.2
Alpha-cellulose content (based on pulp), %	80.0	80.5	79.7
Alpha-cellulose yield, % (based on original wood)	54.0	51.1	51.9
Resistant xylan content, %	7.7	5.6	5.7

This work showed that there was little effect produced by varying the concentration from 4 to 12% sodium hydroxide or by varying the mesh size of the meal from 40-60 mesh to 60-80 mesh. A substantial drop in resistant xylan was obtained by increasing the length of the alkaline treatment to 20 hours on the 40-60 mesh wood meal.

For the coarse wood meal, an increase in alpha-cellulose yield and resistant xylan was obtained. The particle size of a 10-30 mesh wood meal is considerably larger than the 1 mm. average fiber length of aspen-wood so it is probable that relatively few fibers are ruptured in the preparation of 10-30 mesh meal. Just the opposite is true of 40-60 mesh and 60-80 mesh wood meal, and many fibers no doubt are ruptured in the grinding operation. Thus the 10-30 mesh meal behaved more like wood chips than wood meal. This work suggests the possibility that rupturing the fiber structure increases the availability of the xylan to alkali.

KRAFT COOK ON WOOD MEAL

Kraft Cook 7 was performed on 20-40 mesh wood meal using the same procedure and cooking schedule as for kraft Cook 1, except that an 8:1 liquor ratio was used. A portion of the product was bleached and converted to alpha-cellulose by the standard procedures. The results are given in Table XIX in comparison with the corresponding data of the first kraft cook.

TABLE XIX

COMPARISON OF KRAFT COOKS ON WOOD CHIPS AND WOOD MEAL

	Wood Chips	Wood Meal
Yield of unbleached pulp, %	53.7	54.0
Alpha-cellulose yield, % (based on original wood)	45.4	44.8
Resistant xylan content, %	8.1	6.0

This resistant xylan content of 6.0% agrees very well with those obtained for alkaline pretreatment of wood meal. A finer mesh meal was not used for fear of mechanical losses and washing difficulties. Actually this wood meal required one less pass through the Wiley mill than did the 40-60 mesh material used for the work described in the preceding section. Therefore, it is not unreasonable that a kraft cook on a finer-mesh wood meal would produce a pulp with less resistant xylan than 6%. It is unfortunate that a finer-mesh meal was not chosen for the cook.

SODIUM CHLORITE DELIGNIFICATION OF ASPEN SHAVINGS

In order to tie down more closely the difference in behavior between wood chips and wood meal, a material intermediate between these two was investigated. For this purpose thin aspen shavings prepared with a sharp carpenter's plane were used. Penetration of chemicals offered no problem, and yet the number of fibers ruptured during preparation was probably a very minimum. If preservation of the fiber structure is important in obtaining resistant xylan contents, then shavings should behave similarly to chips. This was found to be true.

Chlorite pulp 3 was prepared from 50 grams of the hand-made shavings by the standard procedure. The pulp was then bleached by the one-hour treatment of the standard holocellulose procedure and converted to alpha-cellulose. The results are shown in Table XX.

TABLE XX

CHLORITE PULP 3 FROM ASPEN SHAVINGS

Unbleached pulp yield, %	69.0
Xylan content of unbleached pulp, %	19.4
Bleached pulp yield, %	62.4
Alpha-cellulose content, % (based on bleached pulp)	90.5
Alpha-cellulose yield, % (based on original wood)	56.5
Resistant xylan content, %	13.5

Sixty grams of the aspen shavings were next cold chlorited directly by placing them in 1200 ml. of distilled water, adding 15 ml. of acetic acid and 30 grams of sodium chlorite, and allowing two days' reaction time. An additional 15 ml. of acetic acid and 30 grams of sodium chlorite were then added, and after three days (total reaction time, five days) the shavings were filtered, washed thoroughly by diffusion, and air dried. They were too hard to treat with the Bauer refiner.

The dried, chlorited shavings were then treated with 17.5% sodium hydroxide by the standard procedure. After washing and diffusing in dilute acetic acid and water, the material was converted to a pulp in the Bauer refiner, washed thoroughly, and air dried.

This pulp was then bleached for one hour by the same procedure used previously, and converted to alpha-cellulose by extraction with 17.5% sodium hydroxide. The results are presented in Table XXI.

TABLE XXI

DIRECT COLD CHLORITE OF ASPEN SHAVINGS

Yield of cold-chlorited product, %	91.5
Yield of unbleached pulp by NaOH extraction, % (based on material extracted)	62.4
Yield of unbleached pulp, % (based on original wood)	57.1
Xylan content of unbleached pulp, %	8.8
Yield of bleached pulp, % (based on original wood)	53.9
Alpha-cellulose content, % (based on bleached pulp)	93.8
Alpha-cellulose yield, % (based on original wood)	50.6
Resistant xylan content, %	4.5

The only discussion necessary concerning Tables XX and XXI is the statement that it has again been shown that alkaline treatment prior to chlorite delignification produces a pulp containing a large amount of alkali-resistant xylan, whereas direct chlorite treatment does not. In this respect, the shavings behaved exactly as did the aspen chips, even though penetration was much more rapid than with the chips. Shavings therefore appeared to be an ideal material for further laboratory investigation since they offered no penetration problem but yet gave results comparable with those obtained with chips.

Before the investigation was continued, it was decided to try small shavings made on a power-driven planer, since the preparation of large amounts of shavings with a hand plane was found to be rather tedious. A batch of these shavings was therefore prepared on the power planer in the carpenter's shop. Fifty grams were converted to chlorite pulp 4 by the identical procedure used in obtaining the data of Table XX. The unbleached pulp yield was 66.6%, the alpha-cellulose yield was 57.2%, and the

resistant xylan content of this alpha-cellulose was 13.0%. These were essentially the same results as obtained on handmade shavings, and hence it was decided to use the power planer shavings in further experiments.

EFFECT OF PREHYDROLYSIS ON ASPEN SHAVINGS

The standard holocellulose preparation is carried out at 70-80°C. for three hours in the presence of acetic acid. So-called prehydrolysis may occur during such treatment and may be one reason why an alpha-cellulose prepared from chlorite holocellulose does not have a great deal of resistant xylan. Prehydrolysis experiments were run on aspen shavings treated with water (pH 6.5), dilute acetic acid (pH 3.1), and 0.04 N sulfuric acid (pH 1.5) at 70-80°C. for three hours. After filtering and washing, the shavings were treated with water and 17.5% sodium hydroxide to give a final solution of 8% sodium hydroxide. After a four-hour alkaline treatment, the standard 24-hour room-temperature chlorite delignification was carried out. The pulps produced were Abbé milled and converted to alpha-cellulose with the use of 17.5% sodium hydroxide. A fourth sample of shavings was treated directly with 8% sodium hydroxide in the airdry state and carried through the above procedure. Table XXII contains the results of this work.

TABLE XXII

PREHYDROLYSIS OF ASPEN SHAVINGS

	Prehydrolysis treatment (Type and pH)			
	None --	Water (5.5)	Acetic Acid (3.1)	H_2SO_4 (1.6)
Pulp yield, %	62.8	62.5	62.3	61.0
Alpha-cellulose content (based on pulp), %	84.0	84.6	84.2	83.5
Alpha-cellulose yield, % (based on original wood)	52.8	52.9	52.4	50.9
Resistant xylan content, %	7.3	7.1	6.3	4.7

Hot-water pretreatment caused no substantial reduction of resistant xylan. The acetic acid pretreatment showed a tendency toward producing what might be called a prehydrolysis effect, but it was not as effective as the stronger sulfuric acid hydrolysis. These data established the fact that the action of acetic acid during the standard chlorite holocellulose preparation is not strong enough to cause the large reduction in resistant xylan encountered.

It is difficult to explain the relatively low resistant xylan content of 7.3% obtained without any pretreatment. This type of treatment usually produced pulps which contained 10% or more of resistant xylan. Possibly sample variability or an inherent variability in the procedure was responsible.

The sulfuric acid filtrate contained arabinose and smaller amounts of xylose. This was shown by means of paper partition chromatography.

COMPARISON OF FIBROUS HOLOCELLULOSE AND CHLORITE PULP FROM SHAVINGS

A fibrous chlorite holocellulose was prepared from aspen shavings by a four-hour treatment, using the standard holocellulose procedure. After the treated shavings had been filtered and partially washed, they were converted to a rather harsh pulp in the small Bauer refiner, thoroughly washed, and air dried.

Chlorite pulp 5 was prepared according to the standard procedure with one exception, namely, that 16% potassium hydroxide was used for the four-hour extraction prior to the standard room-temperature chlorite treatment. The reason for this substitution was that the hemicelluloses were to be recovered. The greater solubility of potassium acetate over that of sodium acetate in alcohol has already been discussed. The value of 16% potassium hydroxide was arbitrarily chosen. The hemicelluloses were recovered from the 16% potassium hydroxide filtrate by the standard procedure. The delignified shavings were pulped in the Bauer refiner, washed, and air dried.

The next step in this investigation was to have been the extraction of the hemicelluloses from the fibrous holocellulose and of a second batch of hemicelluloses from the chlorite pulp. The hemicelluloses from the fibrous holocellulose were then to have been compared with the two batches from the chlorite pulp procedure as to viscosity and chemical constitution. This work might have given an indication as to whether or not the direct hot chlorite treatment of wood causes more degradation of the hemicelluloses than the two-stage, resistant xylan-producing procedure.

Before the extraction of the hemicelluloses was carried out, it was decided that so-called test alpha-celluloses would be prepared on a small scale to be sure that the fibrous holocellulose was low in resistant xylan and the chlorite pulp was high in resistant xylan. Departures from the standard procedure consisted of (1) the use of 16% potassium hydroxide instead of 17.5% sodium hydroxide and (2) the elimination of the dilution step prior to filtration. Both of these changes are desirable when the hemicelluloses are to be recovered from the alkaline solution. The results of the work to this point are presented in Table XXIII.

TABLE XXIII

ALPHA-CELLULOSES FROM CHLORITE HOLOCELLULOSE AND CHLORITE PULP USING 16% KOH

	Fibrous Aspen Holocellulose	Aspen Chlorite Pulp 5
Yield of material, %	82.5	62.8
Permanganate no. of material	9.4	5.2
Alpha-cellulose content, % (based on material extracted)	61.9	83.7
Alpha-cellulose yield, % (based on original wood)	51.1	52.6
Resistant xylan content, %	2.6	3.9

As soon as these data were obtained, the emphasis of the experimental program was shifted to a study of the difference in extractive powers of sodium and potassium hydroxides. The 51.1% yield of alpha-cellulose containing 2.6% xylan was expected. However, the alpha-cellulose yield and resistant xylan content from the aspen chlorite pulp should have been considerably higher. At least this was expected in view of the data

previously obtained with 17.5% sodium hydroxide.

This was the first indication that 16% potassium hydroxide produced lower yields of alpha-cellulose which contained much less xylan than did 17.5% sodium hydroxide. Three more test alpha-celluloses were therefore prepared from the same holocellulose and chlorite pulp with 17.5% sodium hydroxide. One extraction was made with dilution to determine its effect on alpha-cellulose yield and xylan content. These results are given in Table XXIV and should be compared directly with those of Table XXIII.

TABLE XXIV

ALPHA-CELLULOSES FROM CHLORITE HOLOCELLULOSE AND CHLORITE PULP USING 17.5% NaOH

	Fibrous Aspen Holocellulose (Without Dilution)	Aspen Chlorite Pulp 5 (Without Dilution)	(With Dilution)
Alpha-cellulose yield, % (based on original wood)	51.1	54.3	53.9
Resistant xylan content, %	5.5	8.3	8.4

Apparently dilution made no difference in the results obtained. The slightly lower alpha-cellulose yield obtained with dilution was within the experimental error and cannot be considered significant. This work established that extraction with 17.5% sodium hydroxide removed less xylan than with 16% potassium hydroxide, and in the case of the chlorite pulp actually resulted in higher alpha-cellulose yields. This is rather surprising since 16% potassium hydroxide on a molar basis is equivalent to only 11.7% sodium hydroxide.

Heuser and Bartunek (32) found that the swelling maximum for sodium hydroxide on cotton cellulose occurs at 15.4% (by weight). Potassium hydroxide was not as effective a swelling agent for cotton as was sodium hydroxide, and its swelling maximum occurred at 25.2% (by weight). Heuser (33) made the observation that the available experimental data show considerable variation for the swelling maximum of cellulose fibers in sodium hydroxide. Older literature gives this concentration as ranging between 16 and 18% (by weight), whereas the range of 10 to 12% is found frequently in more recent investigations. According to Heuser this range of concentration evidently varies with the type of fiber used, the method of purification, and other still unknown factors. Thus, it is very probable that the xylan in aspenwood fibers behaves differently toward various alkalies than does the cellulose in cotton fibers.

As cited in the Historical Review, the findings of Klingstedt that 11% (by weight) and of Heller that 6.5% (by weight) sodium hydroxide exerted the greatest dissolving power on pentosans bear out Heuser's views of the importance of the type of fiber and the method of pulping on the results obtained.

The greater extraction of xylan by potassium hydroxide may be the result of the fact that it has greater penetrating powers than sodium hydroxide. According to Remy (34) the potassium ion carries a much smaller shell of water of hydration than does the sodium ion. This may allow it to penetrate the fiber structure much more readily and therefore dissolve more xylan.

A STUDY OF THE EFFECT OF THE TYPE AND CONCENTRATION OF ALKALI ON RESISTANT XYLAN

FURTHER COMPARISONS OF 17.5% SODIUM HYDROXIDE AND 16% POTASSIUM HYDROXIDE

Action on Bleached Kraft Pulp

A large batch of bleached kraft pulp was prepared from the unbleached kraft pulp of Cook 5 by a one-hour bleach according to the standard procedure. Four alpha-celluloses were prepared therefrom, one of each with dilution and one of each without dilution before filtration, using potassium and sodium hydroxides. The results obtained are shown in Table XXV.

TABLE XXV

ALPHA-CELLULOSES FROM BLEACHED KRAFT PULP

	16% KOH[1]		17.5% NaOH[1]	
	With	Without	With	Without
Alpha-cellulose content, % (based on pulp)	87.2	87.0	91.5	91.6
Alpha-cellulose yield, % (based on original wood)	45.9	45.8	48.2	48.2
Resistant xylan content, %	4.9	4.7	9.2	9.6
Resistant xylan content, % (based on bleached kraft pulp)	4.27	4.17	8.42	8.78

[1] With and without dilution before filtration.

Action on Alpha-Celluloses

The airdry kraft pulp alpha-cellulose containing 8.1% xylan (page 36) and the airdry chlorite pulp alpha-cellulose containing 10.9% xylan (page 50) were re-extracted with the two alkalies by the standard

procedure. Dilution was used before filtration since it was shown to have little effect on the results. These data are presented in Table XXVI.

TABLE XXVI

RE-EXTRACTION OF ALPHA-CELLULOSES WITH KOH AND NaOH

	Alpha-Cellulose From			
	Kraft Pulp		Chlorite Pulp	
	16% KOH	17.5% NaOH	16% KOH	17.5% NaOH
Alpha-cellulose content, % (based on original alpha)	95.3	98.6	88.6	92.6
Alpha-cellulose yield, % (based on original wood)	44.0	45.6	48.2	50.4
Resistant xylan content, %	3.7	6.5	2.8	7.4
Resistant xylan content, % (based on original alpha)	3.51	6.41	2.48	6.85

The data of Tables XXV and XXVI are presented to prove more conclusively what has already been shown, namely: (1) Whether or not the extraction mixture is diluted just before filtration makes no great difference, and (2) 16% potassium hydroxide is more specific in its removal of xylan than 17.5% sodium hydroxide and thereby produces lower yields of alpha-cellulose which contain less xylan than does 17.5% sodium hydroxide. It can be shown that 16% potassium hydroxide is more specific in xylan removal by a tabulation of the difference in yield using the two alkalies *vs.* the difference in resistant xylan content, both based on the original material. These results are shown in Table XXVII.

TABLE XXVII

COMPARISON OF YIELD AND XYLAN DIFFERENCES
USING 16% KOH AND 17.5% NaOH

Alpha-cellulose From	Yield Difference, grams[1]	Xylan Difference, grams
Bleached kraft pulp (with dilution)	4.3	4.15
Bleached kraft pulp (without dilution)	4.6	4.61
Kraft pulp alpha-cellulose	3.3	2.9
Chlorite pulp alpha-cellulose	4.0	4.37

[1] Based on 100 grams of original alpha-cellulose.

These calculations show that in each case almost all the additional material removed by 16% potassium hydroxide was accounted for as a difference in xylan removal.

Another very interesting calculation was made from the data of Table XXVI. The yield on extraction of the kraft pulp alpha-cellulose with 16% potassium hydroxide was 95.3%, or a total loss of 4.7 grams per 100 grams of alpha-cellulose. The xylan content of the alpha-cellulose before extraction was 8.1% but after extraction it was only 3.7%. The xylan loss was 8.1 minus 0.953 x 3.7 or 4.6 grams. Therefore, practically all the material extracted was accounted for as xylan. This point will be discussed further in a later section of the thesis.

A STUDY OF THE ALKALINE PRETREATMENT STAGE OF CHLORITE PULPING

When potassium hydroxide was found to extract more xylan than sodium hydroxide during the alpha-cellulose preparation, it was decided to compare the two alkalies in the alkaline pretreatment stage prior to cold chlorite treatment.

Five batches of aspen chips were extracted with alkali under the following conditions: (1) and (2), 17.5% sodium hydroxide and 16% potassium hydroxide at room temperature for 24 hours; (3) and (4) 4% sodium hydroxide and 4% potassium hydroxide at room temperature for 16 hours followed by boiling at atmospheric pressure for two hours; and (5) 6% sodium hydroxide at room temperature for 48 hours. After the usual filtration, washing, etc., each batch was converted to a chlorite pulp by the standard procedure. Pulping was done in the British disintegrator instead of the small Bauer because the chips were rather soft. After air drying, the pulps were passed through an Abbé mill and converted to alpha-cellulose, using 17.5% sodium hydroxide without dilution. The results are presented in Table XXVIII.

TABLE XXVIII

EFFECT OF VARIOUS ALKALINE TREATMENTS OF ASPEN CHIPS PRIOR TO COLD CHLORITE TREATMENT

	Chlorite Pulp No.				
	6	7	8	9	10
Description of Pretreatment	17.5% NaOH (cold)	16% KOH (cold)	4% NaOH (hot)	4% KOH (hot)	6% NaOH (cold)
Pulp yield, %	66.9	65.0	59.8	61.7	65.5
Xylan content of pulp, %	19.7	17.2	17.2	18.7	--
Alpha content, % (based on pulp)	81.8	84.5	86.0	82.9	83.9
Alpha yield, % (based on original wood)	54.8	54.9	51.4	51.2	54.9
Resistant xylan content, %	10.3	10.1	7.6	7.0	11.6

The results of this work showed:

(1) After alkaline pretreatment with sodium hydroxide and potassium hydroxide, essentially the same alpha-cellulose yields and resistant xylan contents were obtained with the use of 17.5% sodium hydroxide, showing that the difference observed between the two alkalies is restricted to the second, or alpha extraction.

(2) Hot dilute alkaline treatment decreased the resistant xylan content from that obtained with cold concentrated treatment, indicating that more degradation or an increase in availability of the xylan is caused by the hot alkaline treatment.

(3) Boiling 4% sodium hydroxide pretreatment gave an alpha-cellulose yield of 51.4% and a xylan content of 7.6%. This is essentially the same amount of resistant xylan as that obtained from a normal kraft cook with an alpha-cellulose yield of approximately 46% of the wood, i.e., 7.6% x 51.4/46 = 8.5% resistant xylan.

(4) Dilute alkaline pretreatment at room temperature will also yield a pulp with considerable resistant xylan. However, more time is required to obtain good penetration into the chips.

Hot Water Extraction and Hot Bleaching of Chlorite Pulp 7

It was found that the standard hot sodium chlorite bleaching treatment caused a considerable yield loss when applied to the chlorite pulps. For example, the bleaching yield of chlorite pulp 1 was only 91.7% (Table XI). This was a considerably greater loss in yield than would correspond to lignin removal alone. However, it was thought that sodium chlorite treatment could not cause this loss through the degradation of carbohydrate material. Therefore a comparison was made of the effect of hot water, hot dilute acetic acid, and hot bleach liquor on chlorite pulp 7.

One-hour treatments at 70-80°C. were given to three samples of the pulp with distilled water, water plus the amount of acetic acid used in bleaching, and finally the standard sodium chlorite bleach. Alpha-cellulose content and resistant xylan were then determined on the treated pulp by the standard procedure. The results are shown in Table XXIX.

TABLE XXIX

HOT EXTRACTIONS OF ASPEN CHLORITE PULP 7

	Treatment with		
	Water	Dilute Acetic Acid	Acidified Sodium Chlorite
Treated pulp yield, % (based on unbleached pulp)	91.4	91.8	91.6
Treated pulp yield, % (based on original wood)	59.4	59.6	59.5
Alpha-cellulose content, % (based on treated pulp)	86.3	85.6	86.0
Alpha-cellulose yield, % (based on original wood)	51.3	51.1	51.2
Resistant xylan content, %	7.9	8.1	8.0

From these data it can be concluded that the decrease in yield and resistant xylan content is not caused by the sodium chlorite or by the acetic acid but simply by the hot water extraction which takes place in all three cases. Hot water treatment evidently serves to remove a portion of the pulp which is insoluble in cold water and at the same time increases the physical availability of the remaining xylan to alkali. The similarity between these alpha-cellulose yields and resistant xylan contents and those of the hot pretreated pulps of Table XXVIII should be noted; essentially the same product is obtained in the two stages of hot dilute alkaline treatment and cold chlorite delignification as can be obtained in the three stages of cold alkaline treatment, cold chlorite delignification, and hot water extraction.

The plain hot water extraction of the chlorite pulp caused an 8.6% loss in yield. Because of the low lignin contents of chlorite pulps,

most of the extracted material must have been carbohydrate in nature. This water-soluble material was investigated further, and the results will be presented in a later section.

CONCENTRATION STUDIES USING POTASSIUM, SODIUM, AND LITHIUM HYDROXIDES

Aspen chlorite pulp 6 was taken for an investigation of the effect on resistant xylan content of the concentration of alkali used during the alpha-cellulose treatment. Potassium, sodium, and lithium hydroxides were employed, using the standard alpha-cellulose procedure without dilution. The chlorite pulp was first bleached by the standard procedure, air dried, and Abbé milled. The bleached pulp yield was 61.5% based on the original wood (0.669 x 92% bleaching yield), and its xylan content was 17.3%.

The alkali concentrations used (percentage by weight) and the molarities are shown below:

NaOH concentration, %	6	11.7	17.5	24
Molarity	1.60	3.30	5.20	7.57
KOH concentration, %	8	16	24	32
Molarity	1.53	3.28	5.26	7.48
LiOH concentration, %	4	7	10	--
Molarity	1.74	3.14	4.61	--

The results of the experiments are given in Table XXX.

TABLE XXX

CONCENTRATION STUDIES ON ASPEN CHLORITE PULP 6

Part A

NaOH concentration, %	6	11.7	17.5	24
Alpha-cellulose content, % (based on bleached pulp)	80.6	81.6	83.6	83.4
Alpha-cellulose yield, % (based on original wood)	49.6	50.2	51.4	51.3
Resistant xylan content, %	4.1	6.1	8.1	7.0

Part B

KOH concentration, %	8	16	24	32
Alpha-cellulose content, % (based on bleached pulp)	81.3	81.3	79.6	79.8
Alpha-cellulose yield, % (based on original wood)	50.0	50.0	49.0	49.1
Resistant xylan content, %	3.6	3.5	2.1	3.2

Part C

LiOH concentration, %	4	7	10
Alpha-cellulose content, % (based on bleached pulp)	82.9	79.6	79.8
Alpha-cellulose yield, % (based on original wood)	51.0	49.0	49.1
Resistant xylan content, %	5.8	3.4	4.2

These data indicate that sodium hydroxide behaves differently from potassium and lithium hydroxides in its extraction of xylan. For the concentrations employed, the resistant xylan content passed through a maximum at 17.5% sodium hydroxide, but passed through a minimum at 24% potassium hydroxide. Lithium hydroxide also showed a minimum at 7% concentration. Potassium hydroxide was the best of the three alkalies for removing xylan. Apparently, at least for alkaline-prepared aspen pulps, 17.5% sodium hydroxide was the most unsatisfactory choice for determining resistant xylan. It did, however, give higher alpha-cellulose yields than

more dilute solutions of sodium hydroxide. For the sodium hydroxide concentration used, the 6% solution showed the greatest dissolving power on the xylan. This supports Heller's view that 7% sodium hydroxide exerts the greatest dissolving power on xylan. It should also be noted that the xylan content of 2.1% obtained with 24% potassium hydroxide is almost identical with the xylan content of 2.0% for the alpha-cellulose obtained directly from chlorite holocellulose using 16% potassium hydroxide.

The bleached kraft pulp used for the extractions with 17.5% sodium hydroxide and 16% potassium hydroxide (Table XXV) was extracted with 24% potassium hydroxide and 7% lithium hydroxide by the same procedure without dilution. These concentration values were used because they were found to give minimum resistant xylan contents. These data are given in Table XXXI.

TABLE XXXI

ALPHA-CELLULOSES FROM BLEACHED KRAFT PULP

	24% KOH	7% LiOH
Alpha-cellulose content, % (based on bleached pulp)	85.1	86.4
Alpha-cellulose yield, % (based on original wood)	44.8	45.5
Resistant xylan content, %	2.6	4.2

These results agree very well with those for the same alkali concentrations in Table XXX. Potassium and lithium hydroxide again extracted more xylan than did sodium hydroxide, this time from a bleached kraft pulp. This established the fact that aspen chlorite pulps prepared by alkaline pretreatment behave toward the various alkalies in the same

manner as kraft pulps. The main difference in the results obtained was in the alpha-cellulose yields; the more drastic kraft cook produced alpha-cellulose yields of 45-48%, whereas the chlorite pulping procedure gave results of 49-54%, depending upon the alkali type and concentration.

Correns (35) studied the effect of alkali concentration on total removal and pentosan removal from a bleached beech sulfite pulp. He varied the sodium and potassium hydroxide concentrations from about 5 to 18%. He found that the sodium hydroxide at 20°C. always removed more total carbohydrate than did potassium hydroxide at equal concentrations. However, below 10% concentration sodium hydroxide extracted more pentosan than potassium hydroxide, from 10 to 16% concentration potassium hydroxide removed more, and above 16% concentration sodium hydroxide again removed more xylan than potassium hydroxide. His results were almost the opposite of those obtained in this work for aspen kraft pulps and aspen chlorite pulps. This again shows the importance of the type of fiber and method of pulping used.

The differences observed between the behavior of wood meal and wood chips to the chlorite pulping treatment and the dependence of resistant xylan content on the type and concentration of the alkali used for the extraction, are strong evidence that the phenomenon of resistant xylan in alkaline-prepared pulps is related to the physical availability of the xylan to the extracting medium rather than to a chemical combination between xylan and cellulose or to the formation of anhydrohemicelluloses during alkaline treatment.

It was therefore decided to investigate the physical means of

increasing the availability of the xylan to alkali.

FURTHER STUDY OF PHYSICAL EFFECTS

BEATING OF A KRAFT PULP

Meller (23) observed that beating a pulp reduced the resistant pentosan content. Jayme (36) developed a method for measuring the reactivity of a pulp by means of its swelling capacity in water. Using this procedure, Jayme found a considerable increase in the reactivity of pulps during beating.

These findings were tested on the bleached kraft pulp of Table XXV. Twenty-four grams of the pulp were refined in a Lampén ball mill at 3% consistency for four hours. After removal from the Lampén mill, the pulp slurry was thoroughly mixed and divided into two equal portions. One portion was filtered, air dried, and Abbé milled. The second portion was filtered and weighed. Knowing the weights of dry pulp and water present, it was possible to prepare a solution of sodium hydroxide of sufficient strength that, when added to the moist pulp, it would produce the required volume of 17.5% sodium hydroxide. With the above exception, the air-dried and the undried beaten pulp samples were converted to alpha-cellulose by the standard procedure. The yields were not determined. The results are shown in Table XXXII in comparison with the air-dried unbeaten pulp.

TABLE XXXII

EFFECT OF REFINING ON THE RESISTANT XYLAN CONTENT OF A BLEACHED KRAFT PULP

Source of Alpha-Cellulose	Resistant Xylan Content, % (17.5% NaOH)
Unbeaten pulp (airdry)	9.2
Beaten pulp (airdry)	5.4
Beaten pulp (moist)	2.2

These results are in agreement with those of Heller. Thus, xylan can be made more available to sodium hydroxide, probably by a disruption of the fiber structure.

DRY GRINDING OF ASPEN CHLORITE PULP

Chlorite pulp 6 was ground by one pass through a small Wiley mill. The 60-80 mesh fraction was recovered and converted to alpha-cellulose by the standard procedure. The results obtained before and after grinding are compared in Table XXXIII.

TABLE XXXIII

EFFECT OF GRINDING ON THE RESISTANT XYLAN CONTENT OF CHLORITE PULP 6

	Original Pulp	Wiley Mill Ground Pulp
Alpha-cellulose content, % (based on bleached pulp)	83.6	79.7
Alpha-cellulose yield, % (based on original wood)	51.4	49.0
Resistant xylan content, % (using 17.5% NaOH)	8.1	4.5

Again it has been shown that disruption of the fiber structure increases the amount of xylan removed by sodium hydroxide solutions. This fact also helps to explain the difference in behavior encountered between wood chips and wood meal; namely, that alpha-celluloses high in resistant xylan could be obtained from the chips and not from the meal by the chlorite pulping procedure.

EXTRACTION OF MOIST AND AIRDRY BLEACHED KRAFT PULP

The data of Table XXXI show that air drying the beaten pulp caused an increase in the resistant xylan content over that obtained on extraction of the undried pulp. A similar effect may take place on drying an unbeaten pulp. To test this a sample of unbleached kraft pulp 5 was bleached for one hour by the standard procedure. By the same procedure used for the beaten pulp, one fourth of the moist bleached pulp was extracted with 17.5% sodium hydroxide for 45 minutes. The remaining pulp was divided into three equal portions and dried under three different conditions. One portion was conditioned for two days at 70°F. and 50% R.H., a second portion was conditioned for two days at 100°F. and 20% R.H., and the third portion was dried in vacuo at 50°C. The conditioned pulps were stored in moisturetight bottles and finally converted to alpha-celluloses by the standard 17.5% sodium hydroxide procedure. The yields were not determined. The results are presented in Table XXXIV.

TABLE XXXIV

EFFECT OF DRYING ON THE RESISTANT XYLAN CONTENT OF A BLEACHED KRAFT PULP

Source of Alpha-Cellulose	Moisture Content, %	Resistant Xylan Content, %
Undried bleached pulp	—	5.2
Air-dried bleached pulp (70°F., 50% R.H.)	7.1	8.8
Air-dried bleached pulp (100°F., 20% R.H.)	4.3	8.7
Oven-dried bleached pulp (60°C. in vacuo)	0.5	9.2

Air drying of a bleached pulp increases the resistant xylan content, as does oven drying. No dependence on moisture content was evident in the airdry range of 4.3 to 7.1% moisture. Thus, the transition from wet to air-dried pulp increases the resistance of the xylan to extraction much more than does the transition from air-dried to oven-dried pulp.

Jayme (37) applied his method of reactivity measurement to air-dried pulps. He found a decrease in reactivity on air drying to a moisture content of about 10%. This decrease remained constant even after five hours in contact with water and was regarded as irreversible within this period of time. He introduced the term "irreversible cornification" to describe this effect. According to Jayme, with the escape of water, a thicker deposition of the individual polysaccharide chains occurs from the effects of the forces of adhesion and cohesion. This leads to a slight enlargement of the crystalline region. Considerable shrinkage of the fiber occurs. The newly created bonds are in many cases so strong

that the newly entering water is no longer able to disrupt them.

This same view was presented by Whistler (38) who stated: "Presumably when highly hydrated polysaccharide material is slowly air dried, the gradual removal of water molecules allows neighboring polysaccharide molecules or chain segments to come gradually into contact and thereby establish strong secondary unions which later restrain the separation of the molecules, and hence, the penetration of water or solvent molecules."

LOW-XYLAN CONTENT ALPHA-CELLULOSES

From the results of previous experiments, it would seem that the combined use of 24% potassium hydroxide, direct chlorite holocellulose, and fine mesh wood meal should strongly favor the removal of xylan. A holocellulose was therefore prepared from 60-80 mesh wood meal by the standard procedure. An alpha-cellulose was prepared therefrom with the use of 24% potassium hydroxide. For comparison purposes a 24% potassium hydroxide extraction was made on the fibrous chlorite holocellulose from aspen shavings (Table XXIII). The results are given in Table XXXV.

TABLE XXXV

ALPHA-CELLULOSES BY 24% KOH EXTRACTION OF CHLORITE HOLOCELLULOSE

	60-80 Mesh Holocellulose	Fibrous Holocellulose
Holocellulose yield, %	83.0	82.5
Alpha-cellulose content, % (based on holocellulose)	60.3	60.7
Alpha-cellulose yield, % (based on original wood)	50.0	50.1
Resistant xylan content, %	0.8	1.4

This xylan content of 0.8% was the lowest obtained for any of the holocellulose preparations. The value of 1.4% obtained for the fibrous holocellulose was also very low and again shows that the extractive powers of potassium hydroxide are not greatly hindered by the fiber structure, as are those of sodium hydroxide.

It should be noted that both these holocellulose preparations were air dried prior to extraction with alkali. Possibly direct extraction of the moist holocellulose with 24% potassium hydroxide would have removed even more xylan. On the other hand, the low values obtained even with air drying indicate that it does not have an important influence on the resistant xylan content of chlorite holocellulose.

ISOLATION OF A SODIUM HYDROXIDE-RESISTANT XYLAN

Since potassium hydroxide is more specific in removal of xylan than sodium hydroxide, it should be possible to isolate a relatively pure xylan from an alpha-cellulose prepared with sodium hydroxide by giving it a second extraction with potassium hydroxide. The logic of this statement

is supported by a calculation made previously (see page 72) when it was found that the total amount of material extracted from such an alpha-cellulose with 16% potassium hydroxide could be accounted for as a reduction in xylan content. An isolation of this 17.5% sodium hydroxide-resistant xylan was carried out on a portion of the large-scale alpha-cellulose preparation (8.1% resistant xylan) using 24% potassium hydroxide. The material was called "resistant xylan". It was insoluble in water, only partially soluble in 8% potassium hydroxide, and soluble with difficulty in 32% potassium hydroxide.

Fifty grams of the airdry alpha-cellulose (see page 35) were extracted with 1000 ml. of 24% potassium hydroxide for 45 minutes. The alkali was recovered by filtration on a sintered-glass Buchner funnel and poured into 5 liters of ethyl alcohol containing 300 ml. of glacial acetic acid. The precipitate was recovered, washed by means of the centrifuge, and dried overnight in a vacuum oven at 50°C. The alpha-cellulose residue was washed thoroughly and air dried. The yield was 47 grams or 94% of the original alpha-cellulose.

Between 2.8 and 2.9 grams of "resistant xylan" were recovered, of which 0.2 gram was hydrolyzed with 2 ml. of 72% sulfuric acid for one hour, diluted to 5% sulfuric acid, and refluxed for three hours. This hydrolysis solution was chromatographed without neutralization or concentration, using butanol-pyridine-water as the developer. The results of this chromatogram showed that the material actually contained only xylan. Careful examination of the chromatogram under an ultraviolet light revealed no traces of any other sugars or sugar acids.

A xylan analysis of the "resistant xylan" by the standard distillation procedure showed it to consist of 90.5% xylan. The sulfated ash content was 8.9%. There was strong evidence that the ash as present in the "resistant xylan" was potassium bicarbonate. When the xylan was moistened with distilled water, a faintly alkaline reaction to alk-acid paper was obtained; on acidification with sulfuric acid, effervescence was noticed; and finally no acetic acid odor could be detected on acidification and boiling. A logical explanation for the presence of potassium bicarbonate exists in the fact that the potassium hydroxide pellets contained 2.5% carbonate. Neutralization of the alkaline filtrate with acetic acid thus converted the carbonate to bicarbonate but was not strong enough to free it as carbon dioxide. The potassium bicarbonate, since it is insoluble in alcohol, therefore remained as ash in the "resistant xylan". The potassium acetate was washed out because of its solubility in alcohol. This "resistant xylan" therefore contained 10.1% ash, calculated as potassium bicarbonate, and 90.5% xylan.

A pure xylan relatively free of ash could probably be obtained by strongly acidifying the alcoholic mixture with acetic acid prior to recovery of the product. Since this "resistant xylan" was insoluble in water, it could also have been fairly well freed of its ash content by washing with water in a centrifuge bottle and subsequent replacement of the water with alcohol.

Xylan analysis of the alpha-cellulose residue from the above extraction showed it to contain 2.3% xylan, a considerable reduction from the 8.1% before extraction. Hydrolysis and chromatography of this alpha-

cellulose by the standard procedures showed it to contain a small amount of xylan. The total material dissolved in the extraction per 100 grams of original alpha-cellulose was 6 grams (100 minus 94% yield). The xylan dissolved was also approximately 6 grams (8.1 minus 0.94 x 2.3%). This agrees very well with the fact that, except for its ash content, the material extracted was a pure xylan. Evidently all the low-molecular weight cellulose or glucan is dissolved by the 17.5% sodium hydroxide, and the residual cellulose is completely insoluble in 24% potassium hydroxide. Not a trace of glucose could be detected on the chromatogram from the hydrolysis of the "resistant xylan".

The fact that a pure xylan can be isolated by this procedure is convincing proof that potassium hydroxide is better able to penetrate the fiber structure and dissolve out the xylan than is sodium hydroxide.

MISCELLANEOUS RESULTS

ISOLATION OF A WATER-SOLUBLE "XYLAN"

Hot-water extraction of an aspen chlorite pulp prepared by cold alkaline treatment followed by cold chlorite delignification was shown to effect a considerable loss in yield (see page 75). Presumably, a considerable portion of the material extracted is carbohydrate, although some of it may be oxidised lignin. The reason for this yield loss is probably that the hot water exerts a greater dissolving action on the fibers than the cold water used for chlorite treatment and washing. The nature of this hot water-soluble material was investigated cursorily by isolation, hydrolysis, and paper chromatography.

Sixty grams of chlorite pulp 7 were extracted with a liter of distilled water on a steam bath at 80°C. for one hour, filtered, washed with one liter of hot water, and air dried. The extracted pulp yield was 93%; approximately 4 grams of material were dissolved from the pulp. The filtrate and washings were concentrated in vacuo to about 100 ml. and poured into one liter of 95% ethyl alcohol. A very gelatinous precipitate was obtained which was recovered and washed by means of a centrifuge. Three grams of dried material were obtained which was soluble in water and dilute alkali. Two tenths of a gram of the material was hydrolyzed and chromatographed by the procedure described for the "resistant xylan". The chromatogram showed the presence of a large amount of xylose, a considerable amount of a uronic acid, and a faint trace of galactose. A precipitate was formed during hydrolysis; this was probably lignin since it gave a positive Mäule reaction with chlorine water and sodium sulfite.

The material was purified by dissolution in a minimum quantity of hot water, filtration of the solution to remove a small amount of insoluble material, and precipitation of the xylan with an excess of Fehling solution. The gelatinous mass was centrifuged, washed once with fresh Fehling solution, and finally the copper-carbohydrate complex was broken by a thorough washing with methanol containing 5% hydrochloric acid. The product was then washed with acetone containing hydrochloric acid, finally washed free of acid with pure acetone, and dried. Two tenths of a gram was again hydrolyzed and chromatographed. No insoluble lignin precipitate was formed during hydrolysis. The chromatogram showed the material to consist of xylose plus a smaller but definite amount of a uronic acid. No galactose was present. Thus the

material was not a pure xylan but a mixture or chemical combination of xylan and a uronic anhydride.

Since the "resistant xylan" was water insoluble and this material was water soluble, it was decided to compare the specific viscosities of the two materials. This would give a relative measure of their degrees of polymerization. Eight per cent potassium hydroxide was first tried, and $\eta_{sp}/\underline{c}$ was found to be equal to 0.50 for the water-soluble product. However, the "resistant xylan" was only partially soluble in the 8% alkali. The measurements were then repeated with the use of 32% potassium hydroxide. For the water-soluble material a value of $\eta_{sp}/\underline{c}$ = 0.47 was obtained, which is in good agreement with that obtained in the dilute alkaline solution. The "resistant xylan" was finally dissolved in the 32% alkali after considerable shaking. A value of 0.64 was obtained for $\eta_{sp}/\underline{c}$.

According to these values the molecular weight of the "resistant xylan" is not much greater than that of the water-soluble "xylan". Thus the great difference in solubility between the two materials is probably caused by chemical differences rather than any great molecular weight difference. The presence of uronic acid groups in the water-soluble material and their absence in the "resistant xylan" may be sufficient to cause this solubility difference.

Millett and Stamm (39) obtained values of intrinsic viscosity equal to 0.62 for the water-soluble, 0.56 for the 0.5% sodium hydroxide-soluble, and 0.62 for the 5% sodium hydroxide-soluble hemicelluloses from

aspen holocellulose. They concluded that the solubility difference between the three fractions was one of chemical constitution and not one of molecular weight.

ACIDITY MEASUREMENTS ON WOOD AND HOLOCELLULOSE

The difference in acidity between sulfate and sulfite pulps has already been mentioned (page 45). Hot chlorite delignification of wood may increase its acidity by oxidation of the carbohydrate material. The end groups of the hemicellulose molecules could be oxidized to carboxyl groups. Carboxyl groups might also be formed on carbohydrate material at the point of rupture of a lignin-carbohydrate bond. Since the chlorite holocellulose procedure causes a reduction in the viscosity of hemicelluloses as compared to other procedures, such degradation may also result in the formation of additional carboxyl groups. This introduction of additional carboxyl groups in the xylan molecule could greatly increase its solubility in alkali and thus account in part for the low xylan content of alpha-cellulose prepared from chlorite holocellulose.

The failure of extensive sodium chlorite treatment (overbleaching) to reduce the resistant xylan content of kraft and chlorite pulps is not consistent with the above hypothesis. Therefore some explanation must be offered as to why sodium chlorite should oxidize or degrade xylan when applied directly to the wood but not during bleaching of an alkaline-prepared pulp. Possibly the breaking of lignin-carbohydrate bonds by alkaline cooking or alkaline pretreatment makes the lignin much easier to oxidize, while simultaneously the liberated carbohydrates lose their

sensitivity to sodium chlorite oxidation.

An estimate of the increase in free carboxyl groups caused by hot chlorite treatment was made by measuring the organic acidity by the method of Unruh, et al. (40). The method consists of a pH titration after the addition of the wood meal or holocellulose to a 1 N sodium bromide solution until the initial pH of the sodium bromide is again reached. Sodium hydroxide is used in the titration.

Accurately weighed 5-gram samples of wood meal and chlorite holocellulose were soaked in 500 ml. of 0.1 N hydrochloric acid for three hours. The material was then filtered, washed until free of chloride ion with distilled water, and transferred quantitatively to 500 ml. of 1 N sodium bromide solution. Titration was then carried out with 0.0204 N sodium hydroxide to the initial pH of the sodium bromide solution (pH 6.2). Carboxyl groups were calculated as the percentage of -COOH and as the percentage of uronic anhydride. The results are shown in Table XXXVI.

TABLE XXXVI

ORGANIC ACIDITY OF WOOD MEAL AND CHLORITE HOLOCELLULOSE

	Wood Meal	Chlorite Holocellulose
Initial pH of 1 N NaBr	6.2	6.2
pH after addition of material	4.8	3.7
Carboxyl groups, %	0.07	0.46
Carboxyl groups, % (calcd. as uronic anhydride)	0.27	1.80

This is a considerable increase in free carboxyl groups. However, it should be established whether this increase is associated with carbohydrate material or with the residual lignin in the holocellulose.

Institute Method 25 was next used to measure the carbon dioxide evolution from the aspenwood, aspen holocellulose, alkaline-extracted aspenwood, and an aspen chlorite pulp. Table XXXVII contains the results obtained.

TABLE XXXVII

URONIC ANHYDRIDE CONTENT OF ASPENWOOD AND PRODUCTS

	Uronic Anhydride, %	
	Based on Sample Analyzed	Based on Unextracted Wood
Unextracted aspenwood	4.48	4.48
Alcohol-water extracted wood	4.70	4.50
Chlorite holocellulose	6.53	5.55
Thomas holocellulose	7.06	6.11
17.5% NaOH-extracted wood	4.12	3.63
Aspen chlorite pulp	4.66	3.10

These data are evidence of a difference in acidity between direct hot chlorited aspenwood and alkaline-treated, cold chlorited wood. Chlorite holocellulose and Thomas holocellulose both show a considerable increase in carbon dioxide evolution over the aspenwood. This increase is still significant when calculated to the original wood basis. However, both the alkaline-extracted wood and the chlorite pulp prepared therefrom show a definite decrease in carbon dioxide evolution. The apparent increase in uronic acid content of the holocelluloses may be due to oxidized carbohydrate or to the partially oxidized residual lignin in the holocellulose.

In order to determine whether this increased carbon dioxide evolution is caused by oxidized lignin or oxidized carbohydrate, it would be necessary to isolate hemicelluloses by the two procedures and compare their uronic anhydride contents. The isolation from holocellulose represents the usual hemicellulose isolation. The second procedure, however, requires the isolation of two batches of hemicelluloses, the first from the alkaline extract of the original wood or shavings, and the second from the chlorite pulp.

CHEMICAL INVESTIGATION OF ASPENWOOD AND ASPEN HEMICELLULOSES BY PAPER PARTITION CHROMATOGRAPHY

If hot chloriting of wood causes oxidation of the carbohydrate material as well as of lignin, it may be possible to identify different sugar acids in the hydrolyzate of hemicelluloses prepared from chlorite holocellulose from those which are to be found in the hydrolyzate from the original wood. The hemicelluloses used for this investigation were recovered from the 30-50 mesh chlorite holocellulose by the standard procedure.

Two grams of the hemicelluloses were hydrolyzed in 10 ml. of cold 72% sulfuric acid for one-half hour and then in boiling 3% acid for four hours. The sulfuric acid was removed by the use of a basic exchange resin (Dualite A2) to a pH of 6.5, and concentration was carried out in vacuo to a thin sirup which was then investigated by means of paper partition chromatography. Whatman No. 1 filter paper was used throughout the work. The individual sugars in the sirup from the hemicelluloses were identified with the use of butanol-water in a tank located in a hot room controlled at 100°F., and ethyl acetate-acetic acid-water at normal room temperature, as the developers. The latter developer was necessary to obtain separation of

mannose and arabinose. Considerable trouble was encountered in obtaining satisfactory chromatograms because of nonisothermal conditions in the tank which caused evaporation of the solvent from the paper strip. This was solved by thoroughly insulating the tank and elevating it from the floor. Use of the hot room resulted in better and more rapid separations of the sugars than could be obtained at normal room temperature. The chromatograms were removed from the tank, dried, and reinserted in the tank. Two or three such operations with drying in between gave more sharp separations than one long run without removal from the tank. The sugar spots were finally located by spraying the dry paper with aniline hydrogen phthalate.

The following sugars were identified in the hydrolyzate from aspen hemicelluloses by the above procedure; a mixture of known sugars was used to make the positive identification: (1) galactose, (2) glucose, (3) mannose, (4) arabinose, and (5) xylose. The first four sugars were present in small amounts, whereas xylose greatly predominated. A sixth band or spot was identified as glucurone by comparison with a known glucurone spot. A seventh compound was tentatively identified as rhamnose since it matched exactly with a known rhamnose spot. Working with this same aspenwood, Jones (2b) isolated and identified small amounts of rhamnose from a 1 N sulfuric acid hydrolysate of the wood meal. Six sugars and one uronic anhydride have therefore been identified in aspen hemicelluloses.

In order to investigate the acidic components of a hydrolysis mixture, the following procedure was used: 1 gram of hemicelluloses and 2 grams of extracted aspenwood were hydrolyzed with 5 and 10 ml., respectively,

of 72% sulfuric acid for two hours at 18-22°C. and then at boiling 3% acid concentration for four hours. After hydrolysis the acid was removed by a pH titration with barium hydroxide. The break in the titration curve came at pH 3.2, and after filtration the filtrate gave negative tests for barium and sulfate ions. The sugar acids were therefore left in solution. This was then concentrated in vacuo to a sirup which was investigated by paper chromatography.

The hydrolysis mixtures were first chromatographed using butanol-water in the hot-room tank. The hemicelluloses again showed small amounts of galactose, glucose, and mannose, together with large amounts of xylose. The wood meal hydrolysate contained largely glucose and xylose, more mannose than the hemicelluloses, but galactose was obscured by the large amounts of glucose. Cellobiose was also found in the wood meal hydrolysate due to incomplete hydrolysis.

The sugar acids were not moved by the butanol-water mixture and showed up on the starting line. By utilizing this behavior, these acids were then investigated by two-directional chromatography as follows. The unknown hydrolysis mixture was spotted along a line in the center of a 7 inch by 25 inch strip of Whatman No. 1 filter paper. This strip of paper was then placed in the butanol-water developing tank with the starting line near the solvent trough. The extra length of paper was merely allowed to hang out the other side of the trough. The sugars were allowed to move in the usual manner for several days. The paper was then removed from the tank and air dried. The sugars were then located by spraying strips cut from the sides of the paper with aniline hydrogen phthalate; they were then removed from the unsprayed center portion by cutting off the end of the strip at the

indicated location. The sugar acids which stayed on or near the starting line were then separated by inversion of the remaining unsprayed portion of the chromatogram and development in the opposite direction in the ethyl acetate-acetic acid-water tank. This developer moves the sugar acids and permits separations similar to those with the sugars themselves.

After developing the chromatograms for approximately 10 hours, they were removed from the tank, dried, and sprayed. Duplicate chromatograms were run in butanol-pyridine-water before running in ethyl acetate-acetic acid-water. The results of both sets of chromatograms were essentially the same. After the separation of galactose, glucose, mannose, arabinose, xylose, and rhamnose, the ethyl acetate-acetic acid-water solvent separated the sugar acids into at least six different components; the major one was tentatively identified as glucuronic acid. The other components may be either other uronic acids, aldobiuronic acids, or possible aldotriuronic acids. The important thing this work showed was that, by this method of analysis, the original wood and the hemicelluloses prepared after sodium chlorite oxidation contain the same acidic components.

If oxidation of the carbohydrate material to aldonic acids takes place, this method of analysis would not show it because aniline phthalate does not react with aldonic acids. However, alkaline silver nitrate is a satisfactory reagent for spotting aldonic acids. The above chromatographic procedure for the separation of the sugars from the sugar acids was repeated, and the final chromatogram was sprayed with alkaline silver nitrate. Again no differences in acidic components could be detected between the wood meal and hemicellulose hydrolyzates.

Although organic acidity and uronic anhydride determinations showed a difference in acidity between wood meal and chlorite holocellulose, no difference in the acidic components of the hemicelluloses from chlorite holocellulose and those of wood meal could be detected by the methods described above.

GENERAL DISCUSSION

On the preceding pages, the data have been presented which were obtained in a study designed to obtain some of the answers to the problem of the alkali resistance of a portion of the pentosans in aspenwood. The purpose of this discussion is to review the important results of this work in relation to the observations of previous workers and to use the resultant combined picture to develop a hypothesis to explain the mechanisms involved in the resistance of xylan to alkaline extraction. An answer to the original specific thesis problem will also be proposed. Finally, suggestions for future research will be made which are directly related to the problem of resistant xylan and also those which may be classed as possible interesting sidelights.

There is no doubt that pentosans in alkaline-cooked hardwood pulps are very resistant to sodium hydroxide extraction. The amount of this resistant xylan seems to be fairly reproducible among various workers. This author was able to repeat March's work, and values of 8 to 9% resistant xylan were obtained with 17.5% sodium hydroxide. As long ago as 1933 Klingstedt reported 10.9% resistant xylan in an aspen kraft pulp on which 17% sodium hydroxide had been used (see page 11).

It has also been definitely established that this resistant xylan is not affected by strong sodium chlorite bleaching conditions. On the other hand, direct sodium chlorite treatment of wood greatly reduces the resistant xylan content. It is very difficult to explain this behavior without assuming that alkaline treatment chemically alters the lignin-carbohydrate system so that sodium chlorite no longer attacks the xylan.

The kraft cook on chlorite holocellulose established that, even in the absence of most of the lignin, the kraft liquor is relatively mild in its action on xylan, but it does not increase the resistance of xylan to alkali after chlorite treatment. However, the attack on cellulose increased in the absence of lignin. Thus, cold concentrated alkali was found to be more specific to xylan than hot dilute alkali.

From the observations and theories of previous workers the following picture can be formulated (see Historical Review). The xylan and cellulose chains are probably laid down together as the cell grows. Because of their similarity in structural configuration they can both participate in the micelles. The xylan chains are therefore held by secondary valence forces to cellulose, and the incorporation is a sort of mixed crystallization. Any treatment which will reduce these valence forces will favor the removal of xylan. The swelling and penetrating action of alkali is able to disrupt these forces to a certain extent, and the short chain xylan molecules then go into solution. The fact that the alkali must penetrate the fiber walls in order to reach all the xylan emphasizes the importance of the morphological structure of the fibers and how it is affected by various purification treatments. Acidic pulping or prehydrolysis is a very destructive treatment, and on subsequent alkaline swelling many cracks or fissures occur in the cell walls to promote penetration and swelling. Alkaline pulping scarcely attacks the fiber structure, and the difficultly soluble outer layer of the secondary wall does not develop cracks on subsequent alkaline extraction. Instead it retains its spiral structure and resists swelling and probably penetration of the alkali. Thus, the two important factors determining the resistance of xylan are the strength of

the secondary valence forces involved in the cellulose-xylan linkages and the influence of the morphological structure of the fibers as affected by the various pulping or purification procedures. The final amount of resistant xylan depends upon the net effect of the action of the several opposing or supplementary forces acting during the various treatments being given.

The data obtained in this study can be fitted into the above picture. Chlorite pulps prepared from aspen chips and shavings after alkaline treatment behaved very similarly to the kraft and soda pulps with respect to resistant xylan content and its response to various bleaching and extraction conditions. Direct chlorite delignification resulted in low resistant xylan contents. Thus alkaline treatment appears to protect the xylan.

When this chlorite pulping procedure was applied to wood meal, the amounts of resistant xylan obtained were far less than with chips or shavings. When alkaline pulps were refined in a Lampén mill or ground in a Wiley mill, the resistant xylan content was substantially decreased. These experiments showed the importance of retaining the fiber structure. The grinding action cuts the fibers open so that diffusion of alkali into and xylan out of the cell wall can take place through the inner layer of the secondary wall as well as through the outer layer. The refining action in the Lampén mill causes disruption of the cell wall through crushing and fibrillation, thus promoting penetration of the alkali into and diffusion of the dissolved xylan out of the fibers.

The experiments showing the difference in action between sodium and potassium hydroxide support the physical concept of mixed crystallization and secondary valence forces. If the xylan were chemically combined to the cellulose, potassium hydroxide would not be able to remove the xylan more selectively than sodium hydroxide. The isolation of a pure "resistant xylan" with potassium hydroxide is strong evidence of this. A difference in the penetrating or dissolving powers of the two alkalies is probably responsible for their difference in extraction of xylan.

An increase in secondary valence forces between cellulose and xylan as water molecules are removed is an excellent explanation of the increase in resistant xylan content caused by air drying.

The combined action of supplementary forces was employed in producing an alpha-cellulose extremely low in resistant xylan. These supplementary forces were (1) grinding to produce a fine-mesh wood meal, (2) elimination of the protective alkaline pretreatment by employing direct sodium chlorite treatment, and (3) use of 24% potassium hydroxide which was found to be the most satisfactory for xylan removal. Conversely, the high resistant xylan content of kraft or chlorite pulps can be attributed to the supplementary action of (1) the use of chips and of alkaline cooking or pretreatment, both of which result in preservation of the fiber structure, and (2) the use of 17.5% sodium hydroxide in the standard resistant xylan determination, the concentration shown to be the most unsatisfactory for xylan removal.

The following explanation therefore is proposed for the resistance of xylan in kraft pulps to alkaline extraction. The xylan is not chemically combined with the cellulose but is held by secondary valence forces which partially restrain the penetration of sodium hydroxide molecules. Air drying of the unbleached and bleached pulps further increases these secondary forces over those present in the wet pulp. The kraft process preserves the outer layer of the secondary wall which subsequently resists the swelling action of alkali and the diffusion of solvent and solute molecules through it. Finally, xylan is resistant to hot dilute alkali and probably appears in the final pulp in a relatively undegraded form.

The sulfite process, however, greatly degrades the xylan by its hydrolytic action, thus making it extremely soluble in alkali. In addition, the cooking acid attacks the outer layer of the secondary wall so that it no longer resists the swelling action of the extracting alkali.

One of the causes of the low resistance of the xylan in chlorite holocellulose to alkaline extraction is the destruction of the fiber structure during the preparation of wood meal. However, this cannot be the entire explanation because a fibrous holocellulose was also low in resistant xylan content, although not as low as that from wood meal. The following hypothesis is therefore proposed. During direct sodium chlorite delignification of wood, the oxidizing agent splits lignin-xylan bonds. The xylan is also oxidized at these points of cleavage, possibly with the formation of carboxyl groups. It is possible that splitting of these bonds also causes degradation of the xylan. This introduction of carboxyl groups in the xylan molecule or its degradation during chlorite treatment increases its solubility

in alkali. The solubility increase is sufficient to override the effect of any increase in secondary valence forces caused by the air drying of the holocellulose. The increases in apparent uronic anhydride content and organic acidity of the holocellulose on direct chlorite treatment tend to support this oxidation hypothesis (see pages 93-94).

During alkaline cooking or pretreatment, however, this lignin-xylan bond is split by alkaline hydrolysis rather than oxidation. The lignin may then be chemically more reactive toward sodium chlorite as well as more available physically. The free xylan is no longer sensitive to the oxidizing agent, and no carboxyl groups are formed. The decrease in carbon dioxide evolution after alkaline treatment and cold chlorite delignification, the absence of any uronic acid in the isolated "resistant xylan" fraction, and the resistance of the xylan in the chlorite pulps to strong overbleaching by sodium chlorite lend support to this explanation. On subsequent air drying of the bleached pulps the xylan is then strongly bonded to the cellulose by secondary valence forces.

The difference in resistant xylan content of an alpha-cellulose from chlorite holocellulose and one from a bleached kraft pulp using 17.5% sodium hydroxide can therefore be explained by two factors: (1) The chlorite holocellulose was in the form of wood meal, the preparation of which caused a considerable amount of destruction to the fiber structure; the structure of the kraft pulp fibers, on the other hand, was not attacked by the alkaline delignification. (2) Oxidation or degradation of the xylan during holocellulose preparation increased its solubility in the 17.5% alkali; such oxidation or degradation did not occur during bleaching of the kraft pulp.

According to this hypothesis the reason the above-mentioned difference was so great was that the treatments in each case supplemented each other. It can be decreased by proper choice of alkali and by the use of a fibrous holocellulose. Potassium hydroxide was not as greatly hindered in its extractive powers by the fiber structure as was sodium hydroxide. The dependence of the inequality observed on the type and concentration of alkali and on the physical form of the material is shown in Table XXXVIII.

TABLE XXXVIII

DEPENDENCE OF RESISTANT XYLAN CONTENT ON VARIOUS FACTORS

	Bleached	Chlorite Holocellulose	
	Kraft Pulp	Fibrous	Meal
17.5% NaOH-resistant xylan, %	8.1-9.2	5.5	2.3
16% KOH-resistant xylan, %	4.7	2.6	2.0
24% KOH-resistant xylan, %	2.6	1.4	0.8

By using 24% potassium hydroxide for the extraction and retaining the fibrous form in the holocellulose as well as in the pulp, the difference which formed the basis for this thesis is reduced to 2.6 minus 1.4 or 1.2% resistant xylan. It is believed that this difference is still significant and can be explained on the basis of oxidation during chlorite holocellulose preparation.

SUGGESTIONS FOR FURTHER RESEARCH

1. The idea of a lignin-xylan complex being split during the chlorite holocellulose preparation with subsequent oxidation and/or degradation of the xylan is purely speculative. The actual proof or disproof of such a theory would probably require years of experimentation on the specific problem as well as on the general problem of the exact chemical structure of lignin and of lignin-carbohydrate complexes. However, an investigation of the increased acidity and carbon dioxide evolution caused by direct hot chlorite delignification and the corresponding decreases when using alkaline pretreatment and cold chlorite delignification would be important. Any differences in the acidity of the hemicelluloses extracted from the two materials should also be determined and investigated. Greater degradation of the hemicelluloses during chlorite holocellulose preparation might be determined by comparing the viscosities of the above-mentioned hemicellulose fractions.

2. The chlorite pulping procedure should be studied as a possible standard pulping procedure. Runkel (41) proposed a standard pulping procedure to test the natural suitability of plants for paper manufacture, so the idea is not new. His method was similar to the chlorite pulping procedure of this work. It consisted of a dilute alkaline pretreatment of the chips at 100°C., defibration of the softened chips in a rod or ball mill, and finally hot sodium chlorite delignification of the defibered product.

The chlorite pulping method developed for this work offers certain advantages over Runkel's procedure. Both the dilute alkaline pretreatment (6% alkali) and the chlorite delignification are carried out at room temperature

instead of at high temperatures. It is believed that less degradation of the carbohydrate fraction results during these room-temperature treatments. Also the defibering step is not employed until the chips are completely softened by the sodium chlorite. The actual pulping can be accomplished simply by means of a high-speed mixer. Runkel's defibration immediately after alkaline treatment may be rather severe in its action on the fibers.

After preparation of the chlorite pulp the procedure to be employed would be similar to that used by March -- namely, extraction of the pulp with hot water and various concentrations of alkali to find the pulp of maximum over-all strength characteristics that could be obtained. This procedure may produce stronger pulps than the direct chlorite treatment used by March because of the similarity of the chlorite pulps to kraft pulps.

Pulps prepared by the chlorite pulping procedure, Runkel's procedure, March's procedure, and the standard kraft procedure should be compared for their papermaking properties. It is also suggested that both a hardwood and a softwood be used in the work.

3. The chlorite pulping procedure should be investigated as a means of separating hemicelluloses into chemically dissimilar fractions. It is possible that the separations may be entirely arbitrary and of no value in chemically differentiating the hemicelluloses. On the other hand, there is substantial reason to believe that the solubility separations proposed depend to a large extent on differences in chemical constitution as well as on physical availability.

The fractionation should be carried out along the following lines. Dilute alkaline pretreatment of the wood meal will produce the first fraction of hemicelluloses. This direct extraction of hemicelluloses from wood meal has been used in the past; both O'Dwyer (42) and Rogers et al. (43) have employed the method as a rapid means of obtaining hemicellulose preparations. The alkaline-extracted wood meal should then be delignified by the room-temperature chlorite procedure. Subsequent hemicellulose fractions can then be recovered by extraction with hot water, dilute potassium hydroxide (e.g., 5%) and concentrated potassium hydroxide (e.g., 24%). Any of the alkaline extracts which are partially soluble in water can be further fractionated into water-soluble and water-insoluble portions. The hemicellulose fractions obtained should then be compared as to chemical constitution and physical properties. Care should be taken to reduce the ash as much as possible by use of carbonate-free alkali or strong acidification of the alkaline extract with acetic acid.

4. The "resistant xylan" extracted from a kraft pulp alpha-cellulose is an extremely interesting material. A method is thus available for the rapid preparation of a pure xylan in any amount desired. This material itself merits further study.

5. The water-soluble "xylan" prepared by hot-water extraction of a chlorite pulp would be included as one of the fractions in the study proposed above. However, it also should be an interesting material to study. Chromatographically it was shown to consist of xylose and uronic acid units. These may be present as a mixture of xylan and uronic acid chains. However, they may be linked together in the same molecule. Thus the nature of the xylan-uronic acid linkages could be investigated. The uronic acid could also be further identified.

SUMMARY

Bleached kraft and soda pulps were prepared containing 8 to 9% xylan resistant to 17.5% sodium hydroxide extraction. Chlorite holocelluloses prepared from wood meal contained only about 2% of this resistant xylan. Essentially these same results were obtained whether the alpha-cellulose was prepared under nitrogen or the volumetric or gravimetric method of xylan analysis was used.

It was shown that the higher xylan contents as determined by the analytical method were due to true xylan. This was done by means of hydrolysis and paper partition chromatography of the alpha-celluloses.

The resistant xylan content of a kraft pulp could not be reduced by very strong sodium chlorite bleaching of the pulp.

Kraft cooks were performed on chlorite holocellulose and alpha-cellulose from aspenwood and on cotton linters. It was found that resistant xylan was not generated from cellulose by a kraft cook, and that the resistance of the xylan in chlorite holocellulose to alkaline extraction was not increased by kraft cooking.

A soda pulp was shown to contain about the same amount of resistant xylan as a kraft pulp. A sulfite pulp contained very little xylan, and practically all of it was soluble in concentrated alkali. A semichemical kraft pulp contained only about one half as much resistant xylan as the chemical kraft pulp.

Cooks on cotton linters showed that the kraft process causes degradation of cellulose with concomitant reduction of yield, but without any substantial decrease in the alpha-cellulose content of the residue. The sulfite process, on the other hand, caused considerable reduction of the alpha-cellulose content of the product without appreciable loss in yield.

High-yield, low-lignin content pulps were produced from aspen chips and shavings by room-temperature alkaline pretreatment followed by room-temperature sodium chlorite delignification. After hot chlorite bleaching, these pulps contain considerable amounts of 17.5% sodium hydroxide-resistant xylan. This xylan was extremely resistant to overbleaching and re-extraction with concentrated caustic soda. In this respect these pulps behaved exactly like the kraft and soda pulps. The term "aspen chlorite pulp" was used to designate a pulp prepared by this procedure.

This "chlorite pulping" procedure was applied to wood meal under various conditions, but the products were very much lower in resistant xylan content than were the pulps prepared from shavings or chips. These results were attributed to an increase in the physical availability of the xylan to alkali caused by wood meal preparation.

The importance of alkaline pretreatment and the difference in results produced by room-temperature and hot chlorite treatment were studied on chips and shavings. Alkaline pretreatment was found necessary to obtain a pulp containing considerable amounts of resistant xylan. Hot chlorite delignification may cause a certain amount of oxidation or degradation of the xylan not encountered at room temperature, since the resistant xylan contents were lower in pulps prepared after hot treatment as compared to

parallel experiments with room-temperature treatment. However, the temperature of the chlorite delignification was of minor importance as compared to alkaline pretreatment.

The influence of the type of alkali and its concentration on resistant xylan content was studied for a chlorite pulp and a kraft pulp. Sodium, potassium, and lithium hydroxides were compared in these concentration studies. For the concentrations used, 17.5% sodium hydroxide was found to be the least satisfactory for dissolving xylan, whereas 24% potassium hydroxide showed the greatest extracting powers on xylan. Lithium hydroxide fell between sodium and potassium hydroxides with regard to effectiveness in dissolving xylan.

Treatments for increasing the availability of xylan to alkaline extraction were studied. Beating of a wet pulp and grinding of a dry pulp were found to be satisfactory means of decreasing the resistant xylan content. Likewise, a decrease was observed if the bleached pulp was not air dried before the extraction was carried out.

A method was developed for isolating a 17.5% sodium hydroxide-resistant xylan from a kraft pulp. The pulp was first extracted with sodium hydroxide, and then the resistant xylan was recovered by extraction with 24% potassium hydroxide. Except for the presence of about 10% ash, which could have been eliminated by a slight alteration of the procedure, this material was found to be pure xylan. A method was also found for producing an alpha-cellulose extremely low in resistant xylan content. This was done by extraction of a fine-mesh size chlorite holocellulose with 24% potassium hydroxide.

By means of hydrolysis and paper partition chromatography, aspenwood was shown to yield at least six sugars -- galactose, glucose, mannose, arabinose, xylose, and rhamnose -- and the sugar acid glucurone. Those present in the greatest amounts were, of course, glucose from the cellulose and xylose from the xylan.

A hypothesis was proposed to explain the low resistance of xylan in chlorite holocellulose to alkaline extraction.

CONCLUSIONS

1. The alkaline cooking processes produce pulps containing considerable amounts of xylan which is resistant to 17.5% sodium hydroxide. It is not believed, however, that kraft or soda cooks produce resistant xylan from otherwise nonresistant xylan. Rather, the effect is produced through the protective delignification action which takes place and the inability of 17.5% sodium hydroxide to dissolve the xylan from the well-preserved fibers.

2. Grinding to produce wood meal and grinding or refining of a pulp increase the physical availability of the xylan to alkali.

3. It is proposed that oxidation or hydrolysis of the xylan may take place during chlorite holocellulose preparation with the formation of carboxyl groups or degradation of the xylan. If so, this would increase its solubility in the extracting alkali.

4. Resistant xylan is not generated from cellulose during the kraft or soda cook.

5. Resistant xylan is not produced from the nonresistant xylan of a chlorite holocellulose on kraft cooking.

6. Hot dilute alkali is less specific in the removal of xylan from a holocellulose than is cold concentrated alkali. However, the hot dilute alkali removes more non-xylan than the cold concentrated alkali.

7. Sulfite cooking liquor attacks cellulose by a fairly uniform acid hydrolytic cleavage. Thus the product is highly degraded but obtained in high yield because very few water-soluble fragments are produced. Kraft

cooking liquor appears to attack the cellulose chain from the end of the molecule which produces water-soluble compounds as the attack proceeds. However, the residual product, although reduced in yield, is relatively undegraded in the time involved in a kraft cook.

8. Alkaline pretreatment is necessary for obtaining protective delignification during chlorite treatment thus producing chlorite pulps high in resistant xylan content.

9. Strong sodium chlorite bleaching of a pulp containing large amounts of resistant xylan does not measurably reduce the amount of the latter.

10. The use of aspen shavings or chips for the preparation of chlorite pulps leads to products high in resistant xylan, whereas wood meal treated in the same manner does not contain large amounts of resistant xylan. Because of the physical factors involved, a difference results in the chemical composition of the products obtained from chips or shavings and from wood meal. It is recommended that shavings be used for any laboratory comparisons with pulps made from chips. Thus the fibrous form is retained, but penetration problems are minimized.

11. Potassium hydroxide is capable of dissolving more xylan from alkaline-prepared pulps than is sodium hydroxide. Furthermore, the extractive powers of potassium hydroxide are not as greatly influenced by the fiber structure as are those of sodium hydroxide.

12. Air drying of a kraft pulp increases the resistant xylan content, probably by permitting an increase in the secondary valence forces between xylan and cellulose.

13. The resistance of a portion of the xylan in a kraft pulp to alkaline extraction is due in part to physical factors such as the fiber structure and secondary valence forces. However, the insolubility of this "resistant xylan", by reason of its chemical constitution -- namely, its lack of uronic acid groups -- is also responsible in part for the difficulty encountered in extracting it with concentrated alkali.

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APPENDIX

TABLE I

COOKING CONDITIONS FOR KRAFT, SODA, AND SULFITE COOKS

	Kraft Cook 1	Soda Cook	Sulfite Cook
Chemicals used	24% active alkali 33.3% sulfidity	24% active alkali	1.5% combined 5% free SO_2
Water-to-wood ratio	5.5:1	6:1	6:1
Time to 100°C., min.	30	15	60
Time, 100°C. to max., min.	50	45	180
Max. temperature, °C.	176	176	140
Time at max. temp., min.	45	120	180
Time to relieve to zero pressure, min.	10	5	30
Actual cooking time, min.	105	170	390

TABLE II

COOKING CONDITIONS FOR KRAFT COOKS 2, 3, AND 4

	Material Cooked		
	Holo-cellulose	Alpha-Cellulose	Cotton Linters
Active alkali, %	24	24	30
Sulfidity, %	33.3	33.3	33.3
Water-material ratio	8:1	8:1	12:1
Time to 100°C., min.	15	15	10
Time, 100-176°C., min.	45	45	45
Maximum temperature, °C.	176	176	176
Time at max. temp., min.	30	30	45
Time to relieve to zero pressure, min.	5	5	5
Actual cooking time, min.	80	80	95

TABLE III

COOKING CONDITIONS FOR SULFITE COOK ON COTTON LINTERS

Combined sulfur dioxide, %	1.5
Free sulfur dioxide, %	5.0
Water-to-cotton ratio	10:1
Time to 100°C., min.	45
Time, 100°C. to max., min.	120
Maximum temperature, °C.	140
Time at max. temp., min.	180
Time to relieve to zero pressure, min.	30
Actual cooking time, min.	330

TABLE IV

COOKING CONDITIONS FOR KRAFT COOKS 5 AND 6

	Semichemical Pulp (Cook 5)	Soft Kraft Pulp (Cook 6)
Active alkali, %	15	24
Sulfidity, %	33.3	33.3
Water-to-wood ratio	5.5:1	5.5:1
Time to 100°C., min.	15	10
Time, 100°C., to 176°C., min.	50	50
Maximum temperature, °C.	176	176
Time at max. temp., min.	5	100
Time to relieve to zero pressure, min.	5	5
Actual cooking time, min.	60	155